EXCIMER LAMP OXIDANT PRODUCTION AND REMOVAL OF CALCIUM FROM COOLING TOWER WATER

by

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ABSTRACT

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Pulsar UV system (PUV) currently represents the most mature excimer lamp technology. PUV system provides pulsed high-energy blackbody in broadband width. The production, generation and destruction of oxidant radicals by PUV equipment was investigated in this work and modeled by appropriate mathematical expressions. From the mass balance, solving differential equation, this model was derived: concentration versus time for oxidant radical production by PUV equipment. Removal of calcium from the bulk solution and cooling tower water was investigated by using 1) the PUV equipment, 2) the Ozonator and 3) a combination of the PUV equipment and the Ozonator. The removal of calcium was verified. The kinetics of calcium removal from water in all three cases was determined.

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1.0 INTRODUCTION

Conventional, low – intensity, photochemistry includes the photochemical reactions that used a conventional light source and requires a single photon for a reaction to occur. Those light sources can be sunlight, natural room lighting, sunlamps, UV lamps, etc. Low-intensity photochemical reactions are defined as reactions that take place with photon fluxes not exceeding 10^{22} photons/cm^{2}s, while high-intensity photochemical reactions are defined as reactions that take place with photon fluxes in the range of 10^{23} -10^{28} photons/cm^{2}s [Kogelschatz et al., 2000, Salvermoser et al., 2000].

Ultraviolet (UV) light is the name given to electromagnetic radiation in the wavelength range between visible light and X-rays (10 nm - 400 nm or frequencies from 7.5E 14 to 3E 16 Hz). UV light is divided into long and short X-ranges. The long range wavelenght is larger than 200 nm and the short wavelength range is 200 nm [Zhang et al., 1997, Amatepe, 1999].

While a variety of coherent UV sources and incoherent lamps (low-pressure glow discharge in mercury/rare gas mixtures and xenon flashes) are available, only a few high-powered UV sources have as yet become standard equipment for industrial application. A common problem with mercury lamps is that they lack broad emission spectra, so they cannot emit the necessary X radiation consistently. They also produce UV radiation of unwanted wavelengths, as well as visible light. There are applications where current UV treatment systems (that is, the UV sources) are not efficient enough (only a small amount of radiation is emitted in the desired spectral region), or provide the wrong chemistry (emitted radiation spectrum leads to an undesirable chemical reaction pathway). A limited choice of UV sources can result in undesirable side reactions and effects. This can easily be seen, for example, when only a specific target species has to be decomposed out of a multitude of chemical compounds with broadband UV. To improve both

efficiency and selectivity, intense UV radiation sources are needed, such as the excimer lamp [Zhang et al., 1997, Lomaev et al., 2002].

In recent years, various kinds of UV lamps capable of delivering enough power, with high efficiency, have been commercialized. Such UV lamps are now called excimer lamps. They provide excellent performance with high efficiency and low photon cost [Kogelschatz et al., 2000, Amatepe, 1999]. Different types of excimer lamps can be fabricated utilizing repetitively pulsed high power discharges, microwave discharges and dielectric-barrier discharges (silent discharges).

The Pulsar UV (PUV) system provides pulsed high-energy blackbody (blackbody is the electromagnetic radiation that would be radiated from an ideal black body; the distribution of energy in the radiated spectrum of a black body depends only on temperature and is determined by Planck's radiation law) light that radiates predominately in the deep-ultraviolet range at peak power outputs ranging from 3 million watts to 8 million watts in broadband spectrum (a spectrum apparently having all wavelengths over a comparatively wide range, continues wide range of frequencies) [Application of Pulsar's PBUV, 1999, Zhang et al., 2000, Kawanaka et al., 2001]. There are at least several major areas that the PUV technology can be applied: disinfection, photo-degradation of organic contaminants in water, oxidation and removal of metals, removal of MTBE and BTEX and elimination of TOC and Pesticides [Application of Pulsar's PBUV, 1999, Bender 2000].

2.0 LITERATURE REVIEW

2.1 RADICAL FORMATION AND ADVANCED OXIDATON

Advanced oxidations can be accomplished by radical (chain) reactions of mainly atomic singlet oxygen $O(^1D)$, atomic triplet oxygen $O(^3P)$, electronically excited molecular oxygen $0_2(^1\Delta)$ and $0_2(^1\Sigma)$, hydroxyl radicals OH, and ozone. All these species are generated by the excitation or dissociation of molecular oxygen, or the photodissociation of oxygen.

The physical quenching of atomic oxygen, for example, allows the generation of considerable amounts of ozone in air (such as in ozonators). Here the chemical reaction pathway can be extremely complex, but the dominant reaction pathway can be simplified as an initial attack by a radical (mainly hydrogen abstraction reactions) or direct photolysis [Falkenstein, 2001].

The crucial reaction step in these chain reactions is the initial radical attack, which is initiated mainly by the photolysis of molecular oxygen to produce atomic oxygen, ozone, and, in the presence of water vapor, hydroxyl radicals.

This result is further complicated by the fact that molecular oxygen is not only a source of fast reacting atomic oxygen, but is also a sink of atomic oxygen through the formation of relatively slow-reacting ozone. As a result, the advanced oxidation at various oxygen concentrations initially strongly increased the removal efficiency due to the increasing oxygen content. This result indicates that with increasing oxygen concentrations the formation of atomic oxygen increases monotonically.

The example given shows the oxidation of (nonhalogenated) hydrocarbon [Falkenstein, 2001]:

Initial reaction:

$$\text{H-C ...C-H} + \bullet\text{OH} = \text{H-C ... C}\bullet + \text{H}_2\text{O} \quad (1)$$

$$\text{H-C ...C-H} + 0(^1\text{D}) = \text{H-C ... C}\bullet + \bullet\text{OH} \quad (2)$$

$$\text{H-C ...C-H} + 0(^3\text{P}) = \text{H-C ... C}\bullet + \bullet\text{OH} \quad (3)$$

$$\text{H-C ...C-H} + 0_3 = \text{H-C ...C-O}\bullet + \bullet\text{HO}_2 \quad (4)$$

$$\text{H-C ...C-H} + 0_2(^1\Delta) = \text{H-C ... C}\bullet + \bullet\text{HO}_2 \quad (5)$$

$$\text{H-C ...C-H} + h\nu = \text{H-C ... C}\bullet + \bullet\text{H} \quad (6)$$

Second reaction:

$$\text{H-C ... C}\bullet + \text{O}_2 + \text{M} = \text{H-C ...C-O=O}\bullet + \text{M} \quad (7)$$

$$\text{H-C ...C-O=O}\bullet + \text{M} = \text{H-C ... C}\bullet + \text{CO}_2 + \text{M} \quad (8)$$

Subsequent reactions:

$$\text{H-C ... C}\bullet + \text{O}_2 + \text{M} = \text{CO}_2 + \text{H}_2\text{O} \quad (9)$$

The crucial reaction step in these chain reactions is the initial radical attack, which is initiated mainly by the photolysis of molecular oxygen to produce atomic oxygen, ozone, and, in the presence of water hydroxyl radicals. Once the hydrocarbon is converted into a radical, the subsequent reactions with molecular oxygen are endothermic. As a result, the advanced oxidation of hydrocarbons at various oxygen concentrations showed that the removal efficiency initially strongly increases with increasing oxygen content [Falkenstein, 2001].

2.2 PULSAR UV TECHOLOGY

The technology basically consists of pulsed, high-energy blackbody light that radiates predominately in the deep-ultraviolet at peak power levels ranging from 1-million watts to 15-million watts. Photons generated by the Pulsar UV are responsible for the degradation of contaminants in water. The intensity of the pulsed irradiation can produce photons in large numbers which can result in direct photolysis of covalent bonds and cause compounds to fragment. Destruction of the target parent compounds, often referred to as primary degradation, may be sufficient in certain applications such as toxicity removal or odor reduction. Continual photo-degradation can eventually lead to the mineralization of organic compounds to bicarbonate or $C0_2$ [Application of Pulsar's PBUV, 1999, Bender, 1997].

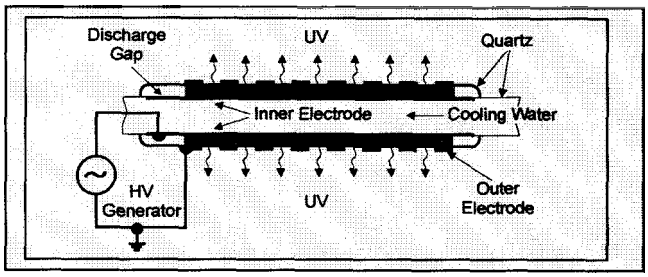

Figure 1: Cylindrical Excimer Lamp Configuration [Falkenstein, 2001]

2.3 ADVANTAGES OF EXCIMER LAMPS

Excimer lamps, due to their simplicity and reliability, present several advantages over lasers, especially when large areas or large volumes have to be treated [Bender, 2000, Bender, 2001].

1) An excimer lamp, with gas pressure lower than that of a laser, reduces self-absorption of radiation from excimer molecules. This increases the operating efficiency and allows the adoption of a

simplerand lower cost electrical power supply system. Theoretical efficiencies as high as 40-50% have been predicted for the UV radiation of Xe2 and Kr2 excimers.

2) Excimer lamps are compact and easier to handle and maintain. Laser systems are relatively large with high capital costs and are expensive to operate and maintain.

3) Excimer lamps produce incoherent radiation; as a result, processing over a large sample area without interference can be performed.

2.4 EXCIMER LAMP POWER PEAK

Figure 2 is the radiation profile over the UV interval versus wavelength [Bender, 2000, Bender, 2001]. Figure 2 shows the blackbody response at the three selected pulse durations or different power inputs. With the increase of power input, maximum peak is increasing and with a rate of controlled repetition, the frequency of power peak can be increased which the feasibility of radical production in the treatment system. At the same time, the excimer lamp continues to produce broad emission spectra. Because of this, excimer lamps can be used for different purposes; they are not limited by wavelength.

Figure 2 shows that 85 % of the radiation energy is in the range between 185 nm and 400 nm, but the other 15 % can still be used for treatments like removal of organic compounds.

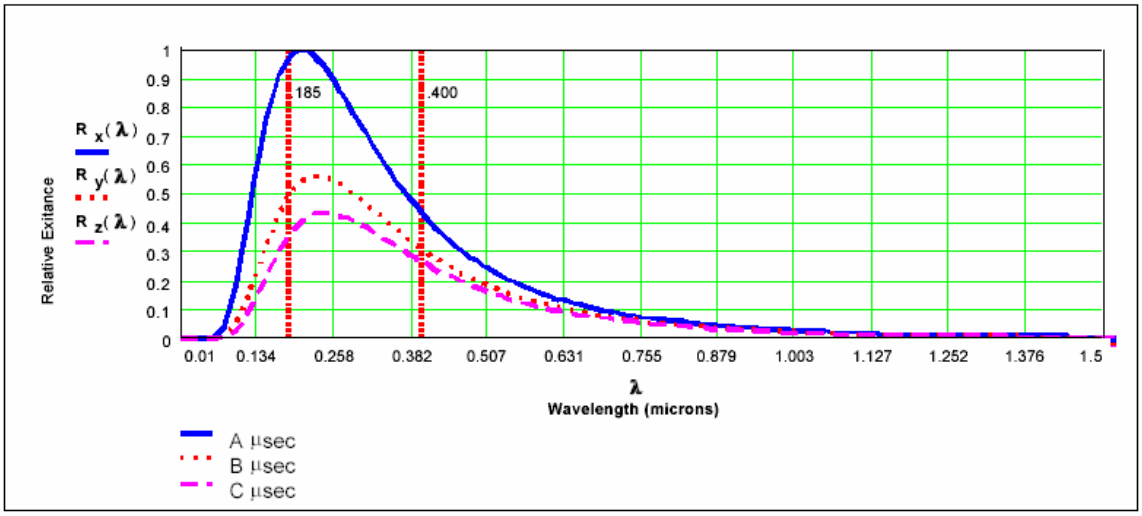

Figure 2: Radiation Profile versus Wavelength [Bender, 2000]

2.5 CHARACTERISTIC OF PUV TECHNOLOGY

The process of photolytic oxidation is a complex series of steps that must be taken in a specific order. Listed below are the primary concerns of photolytic oxidation in the remediation of water [Bender, 2000], [Bender, 20001]:

*1. Lamplife***.** The excimer lamp must be optimized to deliver the maximum amount of useful radiation with good conversion efficiency while still maintaining a useful and long lamplife. Driving the lamp harder to produce even more UV shortens the lamp life considerably and may not be necessary. Careful attention must be paid to optimizing this trade-off between UV intensity and lamplife by adjusting pulse shape, duration, repetition rate, and energy input.

*2. Dosage***.** The contaminant bearing water must receive the proper amount of ultra-violet light. The longer the contaminated water is exposed to the radiation; the greater the dosage, and hence, the longer the free radical chain mechanism can be sustained for complete oxidation.

*3. Quanta Yields***.** The high peak power generated by the lamp over the UV interval determines the number of photons released into the treatment stream. The large quantity of UV photons released into a relatively small volume significantly increases the amount of contaminant species that can be oxidized per pulse.

*4. Coefficient of Absorption***.** Lambert's law describes the decrease in light intensity with distance penetrated into a medium. Decrease levels of TDS and turbidity can solve the problem of light transmission.

*5. Oxidant Production***.** The goal is to ensure that there is enough oxidant available in the water to oxidize the contaminants. This includes considering TDS as contaminants. TDS do absorb ultra-violet light and are likewise oxidized. The optimal amount of oxidant is available with the PUV dose to sustain the free radical chain mechanism. This process is necessary to oxidize the contaminants as completely as possible. In many cases, additional oxidant may not be needed. The water matrix itself or the dissolved oxygen in the water can form such oxidant, but sometimes an additional source of oxidant (if it is available) can significantly improve the process of oxidation.

2.6 WATER DISINFECTION WITH PUV TECHNOLOGY

Water disinfection by UV is a scientifically proven process that kills pathogens and does not create disinfection by-products or taste and odor in drinking water. UV is proven to kill bacteria such as E. Coli, viruses, and other pathogens such as chlorine-resistant *Cryptosporidium* by damaging the DNA molecule, preventing cellular division and eventually causing the pathogen to die [Application of Pulsar's PBUV, 1999].

Two types of microorganisms were tested with the PUV systems. In the first test, Bacillus pumilus spores were used for testing at concentration of approximately 500,000 CFU/ml.

Coffee was added to the water to reduce the light transmission. The exposure time to PUV light was between 3 and 9 seconds. The PBUV system effectively killed the spores by a log reduction of between 4.5 and 4.9. Since the resistant bacterial endospores were used with low matrix transmission and the result suggests that PUV can be highly effective for eliminating bacterial pathogens in drinking water.

The second test was conducted using lamp irradiation in the same manner. In this case, live paramecia were used as the test organisms. With a short contact time of 5-seconds, a total kill of 7,500 cells/ml was observed in the test water. The test data suggest that the PUV system has a great potential for eliminating higher forms of pathogens in drinking water treatment [Application of Pulsar's PBUV, 1999].

2.7 REMOVAL OF MTBE AND BTEX

A significant number of groundwater contaminants result from petroleum products. Among these are MTBE and the aromatic compounds, benzene, toluene, ethylbenzene, and xylene (BTEX). The cleanup target level for benzene and MTBE are often in the range of 1-20 parts per billion (ppb). Both compounds can be effectively degraded by pulsar's PUV to below detection limits. This is particularly significant for MTBE because MTBE often requires high air/water ratio and high adsorbent usage when treated by air stripping or carbon adsorption. Pulsar's PUV can reduce MTBE and benzene cost-effectively and only requires a small footprint. The BTEX destruction data are shown in table 1 [Application of Pulsar's PBUV, 1999].

Table 1: BTEX Removal [Application of Pulsar's PBUV, 1999]

Contaminant	Influent (ppb)	Effluent (ppb)
Benzene	9000	31
Toluene	4100	14
Ethylbenzene	850	3
Xylene	4800	16

2.8 ELIMINATION OF TOC, PESTICIDES AND HERBICIDES

Pulsar UV can fit within sophisticated high purity water production systems often used by food and beverage, bottled water, and pharmaceutical producers. The PUV can achieve both a high degree of disinfection (or even sterilization) and the removal of trace organic compounds (TOC), which are essential for ultra pure water production. For disinfection or sterilization, the PUV does not require high temperature or chemical treatment. Therefore, the method is economical and leaves no undesirable residue such as chlorine and trihalomethanes [Application of Pulsar's PBUV, 1999].

Varieties of pesticides and herbicides have found their way into groundwater and drinking water sources. Surveys have shown that DBCP, EDB, Atrazine, Aldicarb, and Alachlor are detected in well waters in many states. Treatment technologies by PUV reduce contaminants to

less than 1 ppb, or to as low as 0.05 ppb and the process appears to have a high potential for treating contaminated water [Application of Pulsar's PBUV, 1999].

2.9 REMOVAL OF IRON AND MANGANASE

Iron and manganese in groundwater have to be decreased to low levels for drinking or other uses. Most of these two elements are in the soluble or reduced form of divalent ions. Treatment usually involves oxidation by aeration or chlorination to insoluble forms, which can then be filtered. However, the oxidation rates are relatively slow and sometimes incomplete, so the removal efficiencies are not satisfactory. Also, PUV shows that iron can be effectively oxidized and removed by micro-filtration. The PUV treated water also showed lower manganese and turbidity than the chlorinated water [Application of Pulsar's PBUV, 1999].

2.10 OZONE

Ozone [O_3] is an unstable form of oxygen. A component of the much publicized upper-atmosphere ozone layer, this substance form when ultraviolet light (UV) splits [O_2] molecules, allowing some combining with other oxygen molecules to form ozone. Because of its unstable nature, ozone reverts to oxygen within several hours after it forms.

Ozone is one of the most powerful disinfectants available. Whether produced by nature or by man, it can destroy most, if not all bacteria, viruses, and other pathogenic organisms when

properly applied. Ozone is rapidly gaining acceptance as a treatment option as equipment for its manufacture and application becomes more common [Ruisinger, 1996].

Ozonation also contributes to scale control, which is very important for efficient cooling tower operation. Ozone eliminates the biological layer of slime that scale particles typically resist [Ruisinger, 1996].

2.11 REMOVAL OF CALCIUM

Calcium ions are commonly found in natural environments where they often precipitate as carbonate minerals, e.g. calcite and dolomite. Calcium-rich wastewater is a problem for industries due to calcification during downstream processing.

A topic that continues to be of interest to researchers from a variety of fields is the crystallization of calcium carbonate. In addition to its importance by virtue of its prevalence in nature and industry, there is great interest exists in the mechanisms of which chemical systems have control over the construction of $CaCO_3$. The ability of certain chemicals to influence $CaCO_3$ crystallization processes is well known (usually by changing the pH of the system), and its adaptation to prevent the formation of inorganic deposits or scale is a long-time practiced commercial technology [Severtson, 2002].

But the influence of crystal morphology on the formation of $CaCO_3$, demonstrated by [Ruisinger, 1996], increases with increasing ozonization. This is very important for the removal of Ca because ozone can be used along with other systems for the removal of Ca and to improve the precipitation of $CaCO_3$ by improving formation of crystal morphology of $CaCO_3$. Another work [Chandrakanth, 1996] shows that ozone can remove the Ca from water contains particles and Algogenic Organic Matter (AOM).

Ozone will decompose to the very short-lived hydroxyl free radical OH• as follows [Wu et al., 2003]:

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (10)$$

$$HO_2^- + O_3 \rightarrow O_3^- + HO_2 \quad (11)$$

$$O_3^- + H_2O \rightarrow OH\bullet + O_2 + OH^- \quad (12)$$

After some time, very little Ozone molecular can be detected in the solution. Bicarbonate (HCO_3^-) and carbonate (CO_2^{-2}) anions, which may be presented in natural water, are excellent destroyers of hydroxyl free radicals. Therefore, when ozone decomposes to hydroxyl free radicals, free radicals can react with bicarbonate or carbonate anions readily. This reaction destroys the original equilibrium state in the solution by changing the composition and properties of the solution. The destruction of the original equilibrium state of the solution by hydroxyl free radicals due to the decomposition of ozone becomes the dominant process in water.

3.0 MATERIALS AND METHODS

PUV light source Pulsar Model RipTide-5000, manufactured by Pulsar UV Technologies, Inc. was used. The Pulsar Model RipTide-5000 is a 5 kilowatt Advanced UV water treatment system that produces pulsed blackbody ultraviolet light. By adjusting input energy (Joules), voltage (Volts, can be adjusted in increments of 25 V, range 0-5000 V) and pulse duration (Hz or pulse per second, can be adjusted in increments of 0.1 Hz, range 0.1-10 Hz), input data was designed for the experiment.

Figure 3: PUV Experimental Equipment

3.1 DESCRIPTION OF RIPTADE-5000

The system consists of a console, a reaction chamber and a cooling system. All three main parts are connected and the reaction chamber and cooling system receive power from the high voltage power supply in the console.

3.1.1 Console Description

The console consists of a high voltage power supply and a control panel. It also contains an on/off key switch and an emergency off switch. The dimensions of the console are 60" x 48" x 33" and the weight is 525 lbs. The electrical utilities requirements are 208 VAC, 60 Hz, 70 and single phase. The control panel is located on top of the high voltage power supply console and contains all the controls required by the operator to regulate and monitor the system operating parameters: power, pulse rate, voltage and system status.

Figure 4: Console and Power Supply

3.1.2 Reaction Chamber

The reaction chamber is a 1.75 gallon stainless steel cylindrical chamber that houses the flashlamp and the treatment water. The Flashlamp produces a UV band in the range of 185-400 nm and the lamp power is 5000 watts. Both bases of the reaction chamber are connected with electrical cables to the console (power supply), and in that way the flashlamp receives the necessary energy supply. At the same time, the reaction chamber has two more connections, water hoses directly connected to the cooling system for the input/output of cooling water that keeps the system from becoming overheated. The reaction chamber has two more connections for the input/output of treatment water.

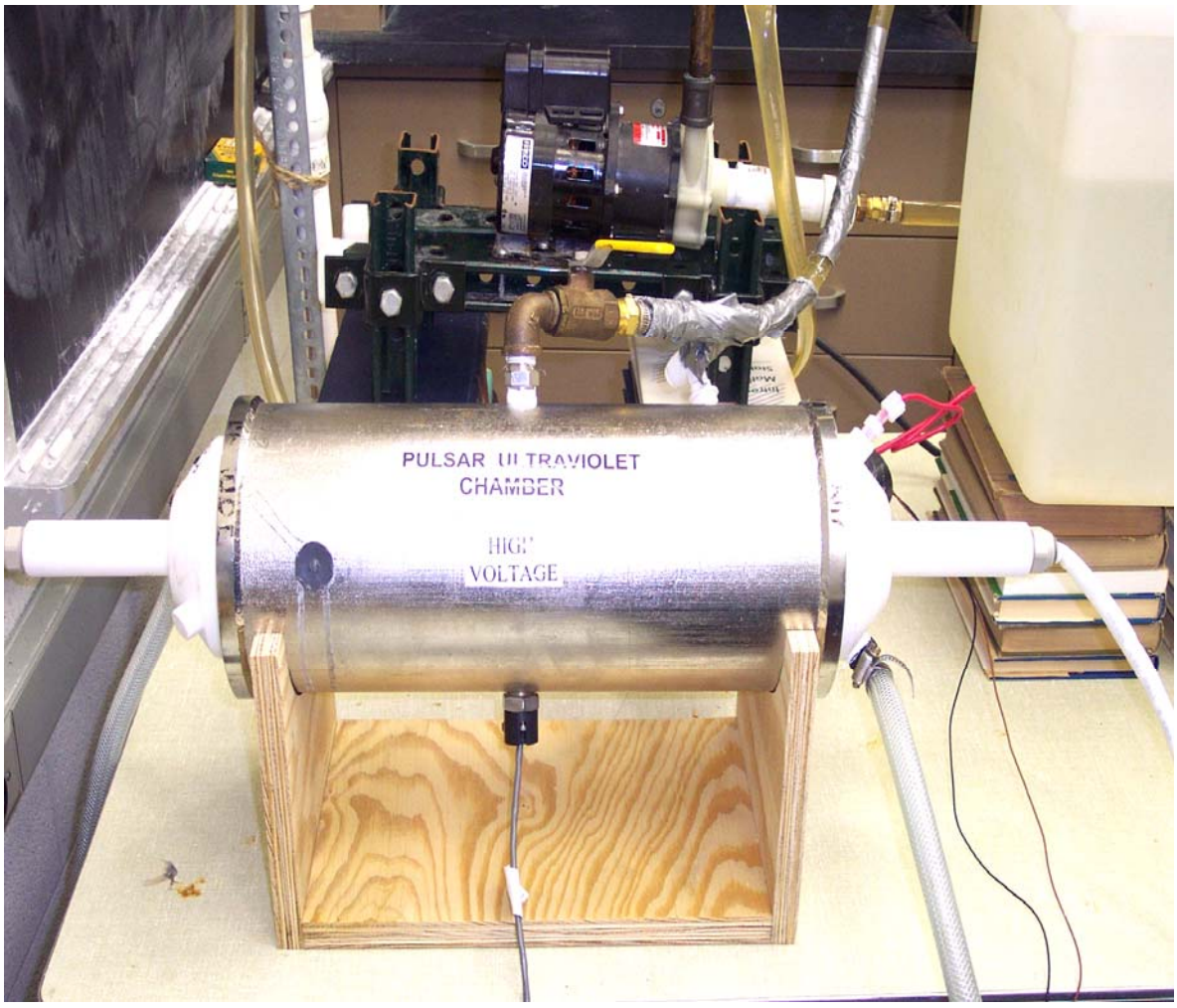

Figure 5: Reaction Chamber

3.1.3 Cooling System

The purpose of the cooling system is to cool the flashlamp and the treatment water and to protect the system from becoming overheated. The temperature of the water at the chiller is adjusted to 4 °C all the time. The dimensions of the chiller are 40” x 28” x 24” and the weight 110 lbs. The chiller is connected to the console with electrical cables to receive energy from the power supply.

Figure 6: Cooling System

3.2 OZONATOR

An Ozonator is a device that produces ozone, using electrical charges to transform oxygen to ozone. The Ozonator used in this work is OREC MODEL # O3B1-O, manufactured by Ozone Research and Equipment Corporation. The Ozonator incorporates 15,000 volts and pressure of gas from 1 to 30 psi. The Ozonator has an input connected with the oxygen (air) cylinder and an output where produced ozone exhausts out and can be used for treatment (usually with water). At the same time, the Ozonator has input/output connections for cooling water that come from the drinking water system (tap water) and protect the Ozonator from overheating. Maximum allowable outlet temperature is 80 F. It is recommended that approximately 3 liters/minute water be allowed to flow in order to maintain the water outlet temperature. The Ozonator has a control panel with a voltmeter (range of voltage 0-100 V), a voltage switch control, an amperemeter (range of 0 – 10 A), an air (oxygen) flowmeter and on/off switch.

4.0 RESULTS AND DISCUSSION

This section contains results from several sets of experiments. The first set of experiments was designed to determine the kinetics of oxidant production by PUV equipment. The second set of experiments was designed to show that oxidant produced by PUV equipment and ozone can remove Ca from a bulk solution of water and from cooling tower water.

4.1 KINETICS OF OXIDANT PRODUCTION BY PUV

The design of this experiment is given in Figure 7. It is a closed system. The treatment fluid is tap water and that fluid is in the reservoir. Volume of the reservoir is 35 liters. Water from the reservoir is transported by the pump to the reaction chamber. In the reaction chamber, the water receives power input from the PUV lump and that energy produces oxidant radicals in the water. It wasn't determined the chemical nature of the oxidant mixture in water, produce by the PUV equipment. All oxidant concentrations in this set of experiments were represented as meq/l of oxidants as oxygen. The volume of the reactor chamber is 1.75 gallons and the flow rate for this set of experiments is 0.3 gal /min. The detention time is about 5.8 min. Before beginning this experiment, a control (blank) experiment was conducted and no oxidant radical concentration or concentration of oxidant were detected in the treatment water.

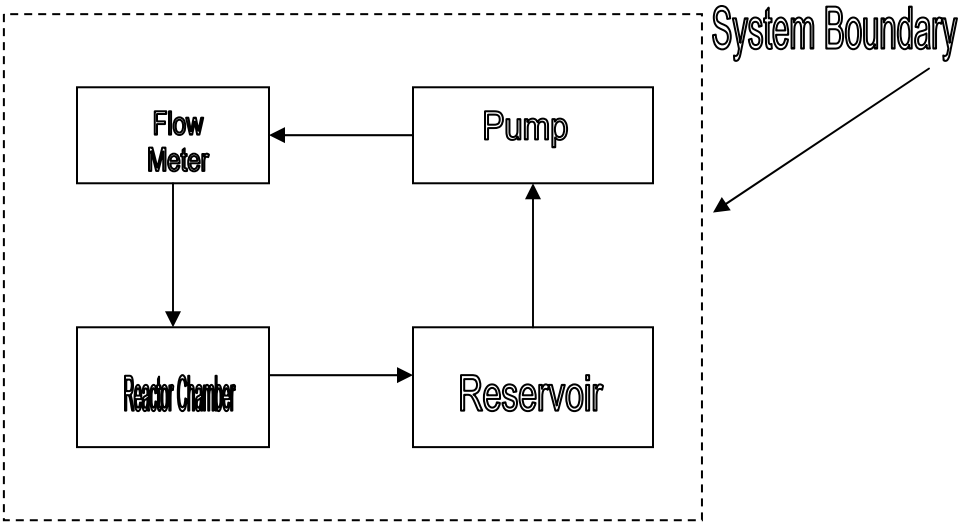

Figure 7: Experiment Design for Using PUV Equipment

Material balance of oxidant for this system:

$$[\text{Rate of Accumulation}] = [\text{Input}] - [\text{Output}] + [\text{Rate of Generation}] - [\text{Reduction}] \quad (13)$$

$$[\text{Input}] = 0 \quad (14)$$

$$[\text{Output}] = 0 \quad (15)$$

From (13), (14), and (15):

$$[\text{Rate of Accumulation}] = [\text{Rate of Generation}] - [\text{Reduction}] \quad (16)$$

The Purpose of this experiment was first, to determine the mathematical models for the rate of generation and reduction from the experimental data, and second, to determine the total mathematical model for the entire system, and last, to compare the derived model with the experimental data. Oxidant reduction probably occurs because of two parallel processes in water: decay and decomposition. Decay is natural chemical process for oxidant radicals in water and decomposition occurs because oxidant radicals react with materials in tap water (TOC, metals, etc.). It was run three same experiment.

4.1.1 Oxidant Radical Production by PUV Equipment

The first step to determine the kinetics is to measure of oxidant radical concentration versus time. The experiment's design is to find oxidant radical concentration versus time for different power inputs (voltage and frequency). Samples are taken from the reservoir every five minutes. The concentrations were measured using the Iodometric Standard Method [Standard Methods, 1998]. Oxidant radical concentrations are calculated from this formula:

$$\text{meq of Oxidant as } O_2 \text{ / L} = \frac{(A+B)*N*1000}{(ml \cdot sample)} \tag{17}$$

A = ml titration for sample

B = ml titration for blank

N = normality of $Na_2S_2O_3$

The normality of $Na_2S_2O_3$ used for this experiment is 0.001 N, and the sample volume is 200 ml. The results of the experiment are given in Table 2 and Table 3 and represented in Figure 8 and Figure 9.

Table 2: Oxidant Concentration versus Time at Varying Energy Input Levels at 4 Hz

Time min	Conentration meq/l 4 Hz, 2000V			Conentration meq/l 4 Hz, 2600V		
	exper 1.	exper 2.	exper 3.	exper 1.	exper 2.	exper 3.
0	0	0	0	0	0	0
5	0.0740	0.0760	0.0780	0.0970	0.0990	0.0990
10	0.0800	0.0810	0.0820	0.1048	0.1055	0.1060
15	0.0848	0.0855	0.0855	0.1180	0.1200	0.1230
20	0.0907	0.0915	0.0919	0.1400	0.1435	0.1450
25	0.0945	0.0945	0.0949	0.1490	0.1490	0.1520
30	0.0954	0.0955	0.0956	0.1500	0.1505	0.1515
35	0.0954	0.0955	0.0956	0.1500	0.1505	0.1515
40	0.0954	0.0955	0.0956	0.1500	0.1505	0.1515
Time min	Conentration meq/l 4 Hz, 3200V			Conentration meq/l 4 Hz, 3800V		
	exper 1.	exper 2.	exper 3.	exper 1.	exper 2.	exper 3.
0	0	0	0	0	0	0
5	0.1125	0.1135	0.1139	0.1215	0.1225	0.1235
10	0.1228	0.1235	0.1235	0.1285	0.1295	0.1299
15	0.1402	0.1415	0.1425	0.15	0.1505	0.1525
20	0.1600	0.1630	0.164	0.1755	0.1775	0.1775
25	0.1881	0.1885	0.1889	0.196	0.1965	0.1985
30	0.2000	0.2010	0.2080	0.22	0.2215	0.2235
35	0.2000	0.2010	0.2080	0.22	0.2215	0.2235
40	0.2000	0.2010	0.2080	0.22	0.2215	0.2235

Table 3: Oxidant Concentration versus Time at Varying Energy Input Levels at 8 Hz

Time min	Conentration meq/l 8 Hz, 2000V			Conentration meq/l 8 Hz, 2600V		
	exper 1.	exper 2.	exper 3.	exper 1.	exper 2.	exper 3.
0	0	0	0	0	0	0
5	0.126	0.128	0.129	0.144	0.145	0.146
10	0.154	0.156	0.157	0.195	0.197	0.199
15	0.170	0.180	0.190	0.208	0.215	0.225
20	0.200	0.205	0.209	0.233	0.234	0.235
25	0.216	0.217	0.219	0.256	0.258	0.259
30	0.228	0.229	0.231	0.260	0.260	0.262
35	0.228	0.229	0.231	0.260	0.260	0.262
40	0.228	0.229	0.231	0.260	0.260	0.262

Time min	Conentration meq/l 8 Hz, 3200V			Conentration meq/l 8 Hz, 3800V		
	exper 1.	exper 2.	exper 3.	exper 1.	exper 2.	exper 3.
0	0	0	0	0	0	0
5	0.142	0.155	0.165	0.160	0.163	0.164
10	0.210	0.210	0.212	0.220	0.221	0.223
15	0.226	0.229	0.230	0.240	0.241	0.242
20	0.264	0.265	0.268	0.278	0.279	0.281
25	0.278	0.279	0.280	0.290	0.292	0.293
30	0.281	0.282	0.283	0.315	0.316	0.317
35	0.281	0.282	0.283	0.315	0.316	0.317
40	0.281	0.282	0.283	0.315	0.316	0.317

Time min	Conentration meq/l 8 Hz, 4200V			Conentration meq/l 8 Hz, 4800V		
	exper 1.	exper 2.	exper 3.	exper 1.	exper 2.	exper 3.
0	0	0	0	0	0	0
5	0.167	0.169	0.170	0.173	0.175	0.176
10	0.232	0.234	0.235	0.242	0.243	0.245
15	0.250	0.250	0.252	0.260	0.262	0.263
20	0.284	0.286	0.287	0.290	0.295	0.302
25	0.300	0.305	0.307	0.310	0.310	0.313
30	0.320	0.320	0.321	0.324	0.324	0.325
35	0.320	0.320	0.321	0.324	0.324	0.325
40	0.320	0.320	0.321	0.324	0.324	0.325

It can be concluded from Figure 8 and Figure 9 that with increasing power input (voltage, frequency), the production of oxidant radical concentration increases also. At the same time, for all range of data it can be seen that after some time oxidant concentration plateaus, indicating the

system is in steady state. For this experimental design, material balance at steady state: [Rate of Accumulation] = 0, [Rate of Generation] = [Reduction].

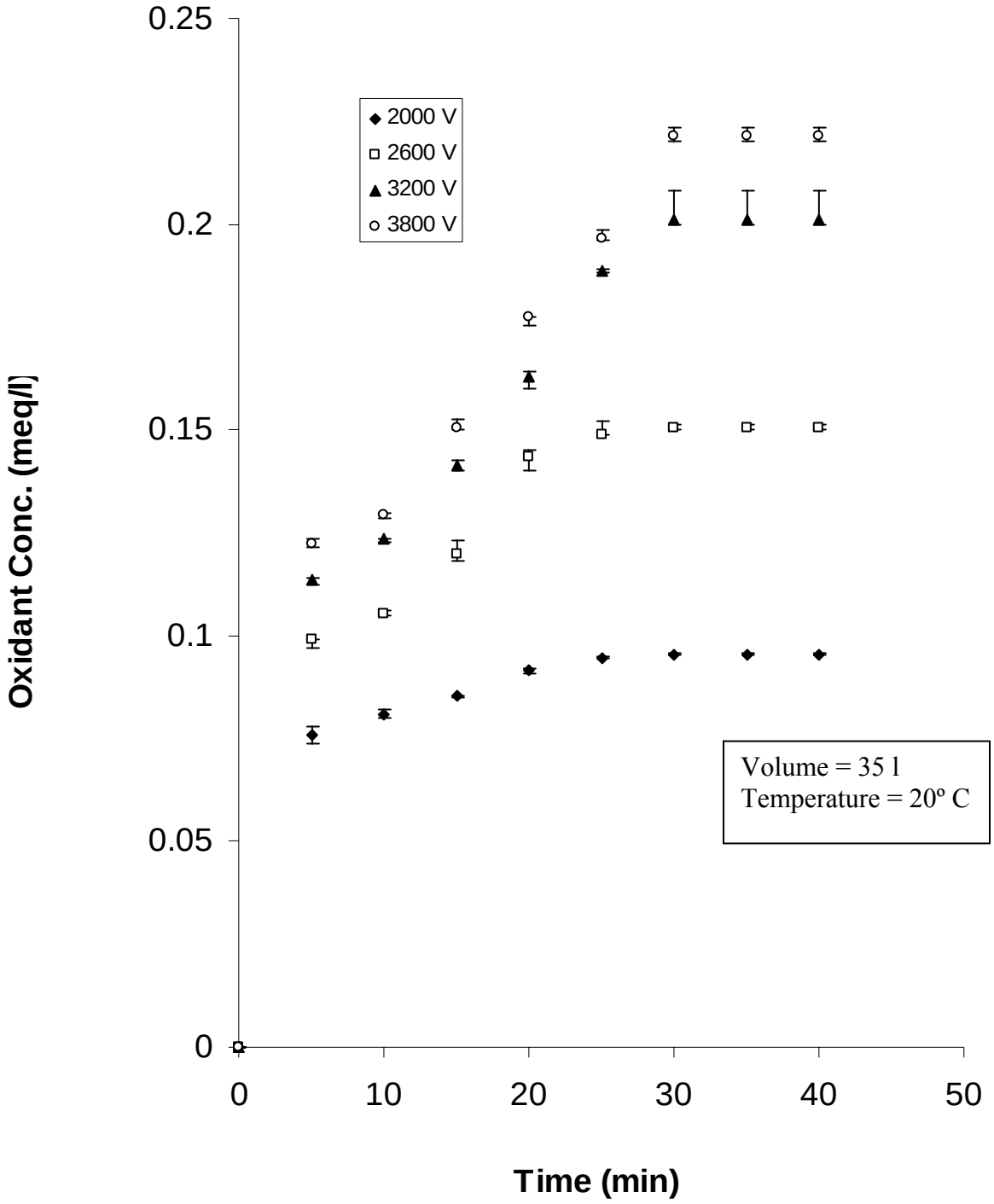

Figure 8: Oxidant Concentration versus Time at Varying Energy Input Levels at 4 Hz

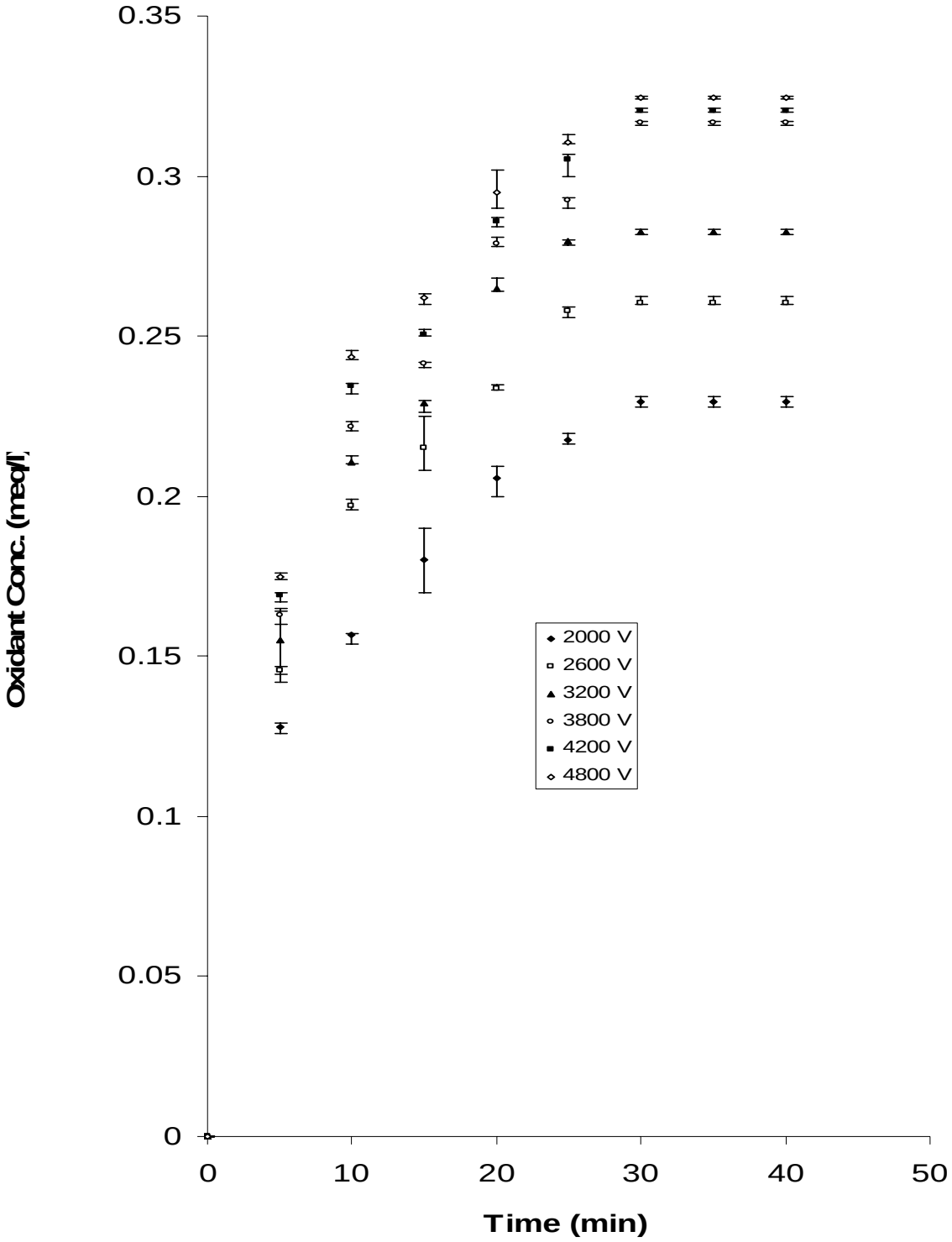

Figure 9: Oxidant Concentration versus Time at Varying Energy Input Levels at 8 Hz

4.1.2 Determination of Oxidant Reduction Kinetics

The oxidant reduction was measured experimentally, and from the fit with experimental data, the coefficient of decay (k_d) was determined, as was the order of decay reaction (n).

For this purpose, the experiments were run at 8 Hz and 4800 V (maximum power available), and when the system reached steady state (after 30-35 min.), the input of energy was stopped. At that moment, samples began to be taken from the reservoir every two minutes. The measured oxidant concentration data are provided in Table 4. Data from Table 4 are represented in Figure 10. As we see from Figure 10, decreases in concentration versus time show a not linear function and it can be written in the form:

$$[\mathrm{Re}\,duction] = \frac{dC}{dt} = k_d * C^n \tag{18}$$

k_d = coefficient of reduction ($min^{-1} * [l/meq]^{n-1}$)

C = oxidant concentration (meq/l)

n = order of reduction reaction

t = time (min)

The solution for differential equation (17) for $C = C_0$ and $t = t_0$:

$$C^{1-n} - C_0^{1-n} = (1-n) * k_d * (t - t_0) \tag{19}$$

C_0 = starting oxidant concentration (meq/l)

t_0 = time at start of experiment (min)

A curve fitting approach was used for equation (19) to find the best fit for slope k_d (1-n) and "n" and data are represented in Figure 11. If was plotted $C^{1-n} - C_0^{1-n}$ versus $(t-t_0)$, change (try and error for different value of n to find best R^2) and fit 'n' (order of reduction) to provide the best fit of data (line). Assigning 'n' a value of 0.5 that was the coefficient value that best fit

experimental and 0.0342 was the value calculated for k_d (coefficient of reduction). When those values are placed in equation (18), the following results are calculated:

$$\left[\text{Re}\,duction\right] = \frac{dC}{dt} = -0.0342 * C^{0.5} \tag{20}$$

Table 4: Oxidant Reduction versus Time

	exper. 1	exper. 2	exper.3
Time (min)	meq/L Oxid	meq/l Oxi	meq/l Oxi
2	0.345	0.357	0.367
4	0.301	0.311	0.322
6	0.25	0.261	0.268
8	0.242		0.255
10	0.227	0.235	0.246
12	0.172	0.175	0.181
14	0.149	0.156	0.167
16	0.123	0.127	0.139
18	0.091	0.094	0.099
20	0.063	0.07	0.078
22	0.051	0.057	0.059
24	0.04	0.041	0.048
26	0.032	0.038	0.039

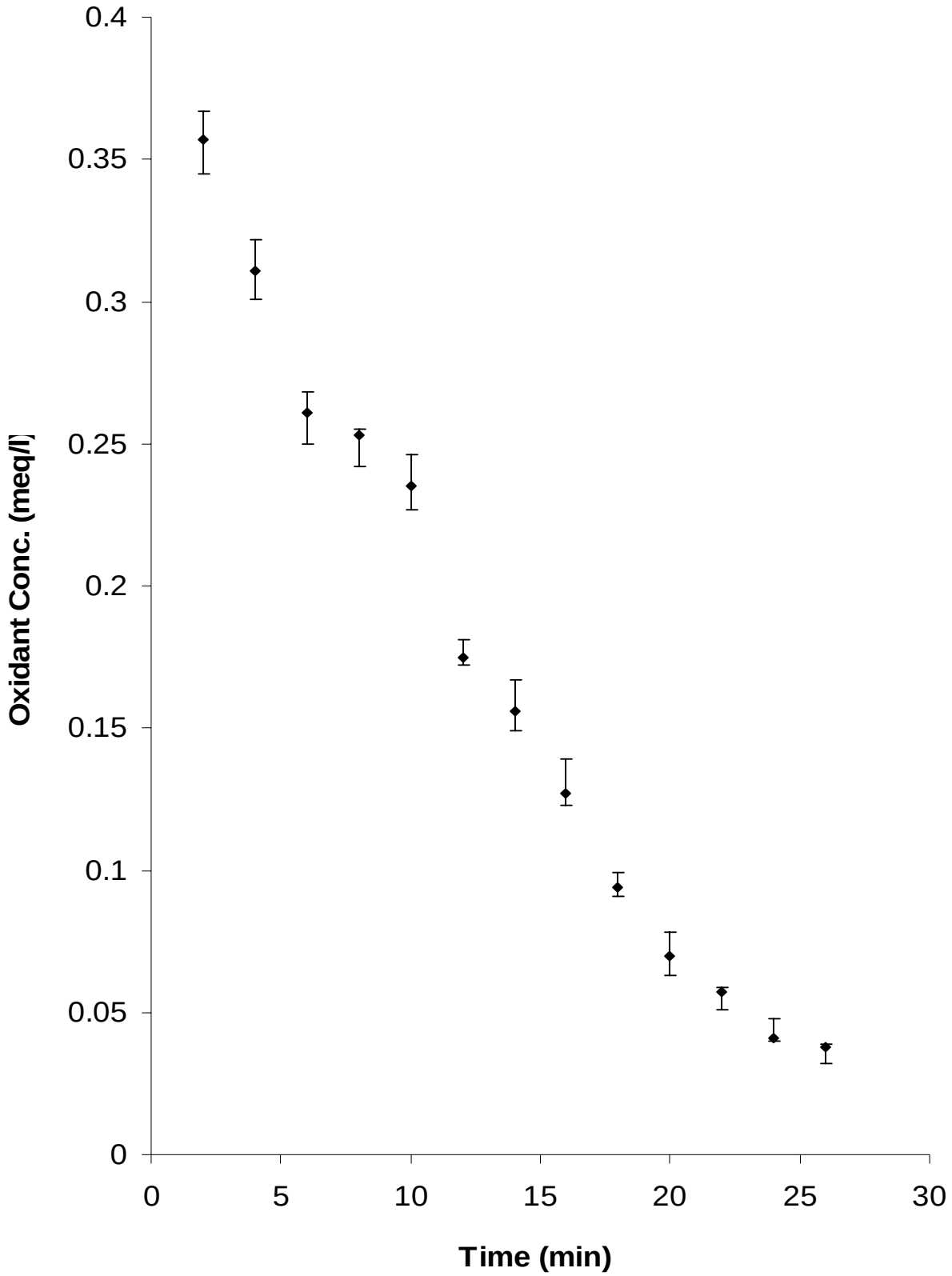

Figure 10: Oxidant Reduction versus Time

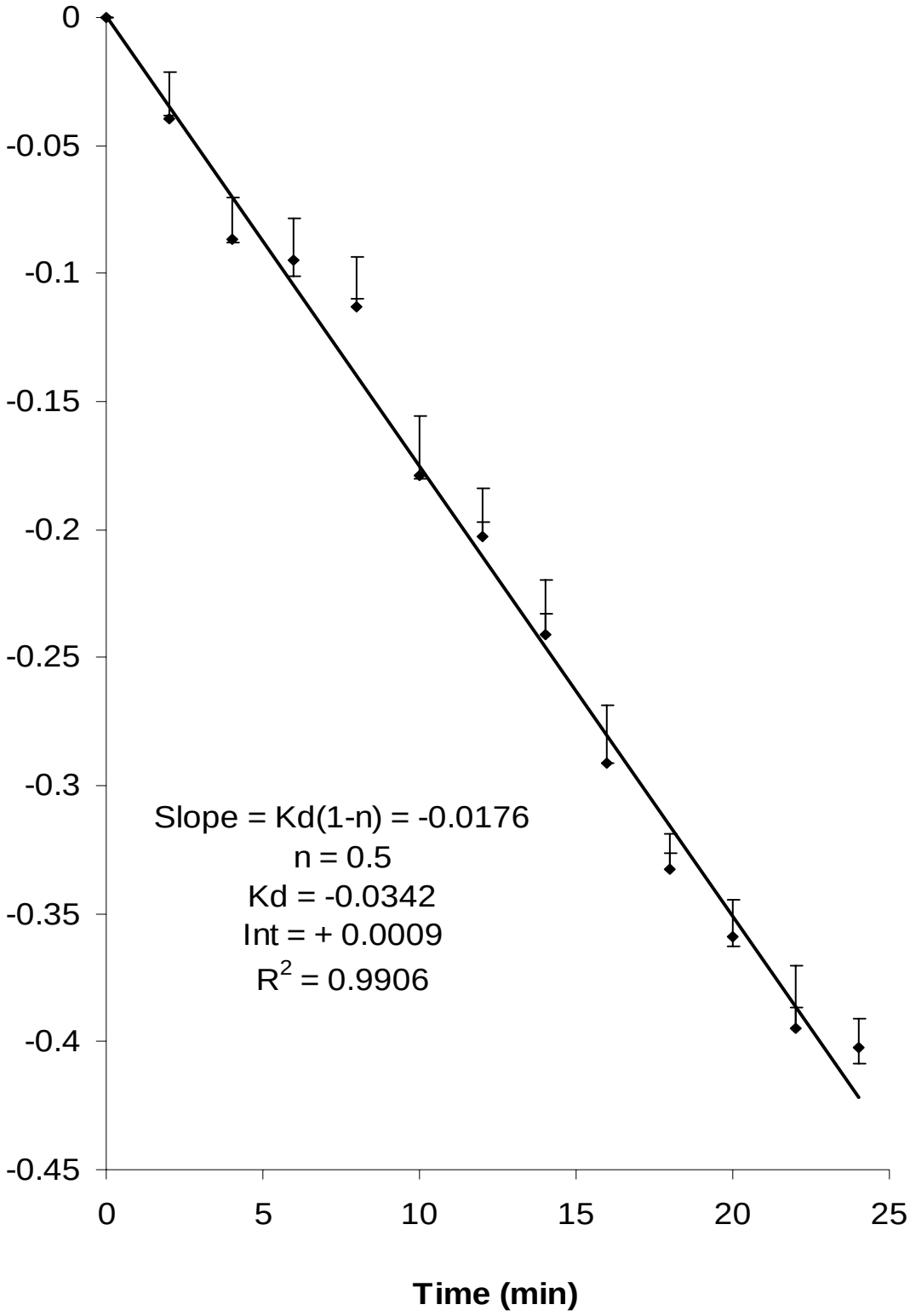

Figure 11: Determination of Coefficient of Reduction by Fitting Experimental Data

Figure 12 places side by side the mathematical models (best fitting) and the experimental data. We can conclude that this model is a good fit and approximation for the experimental data.

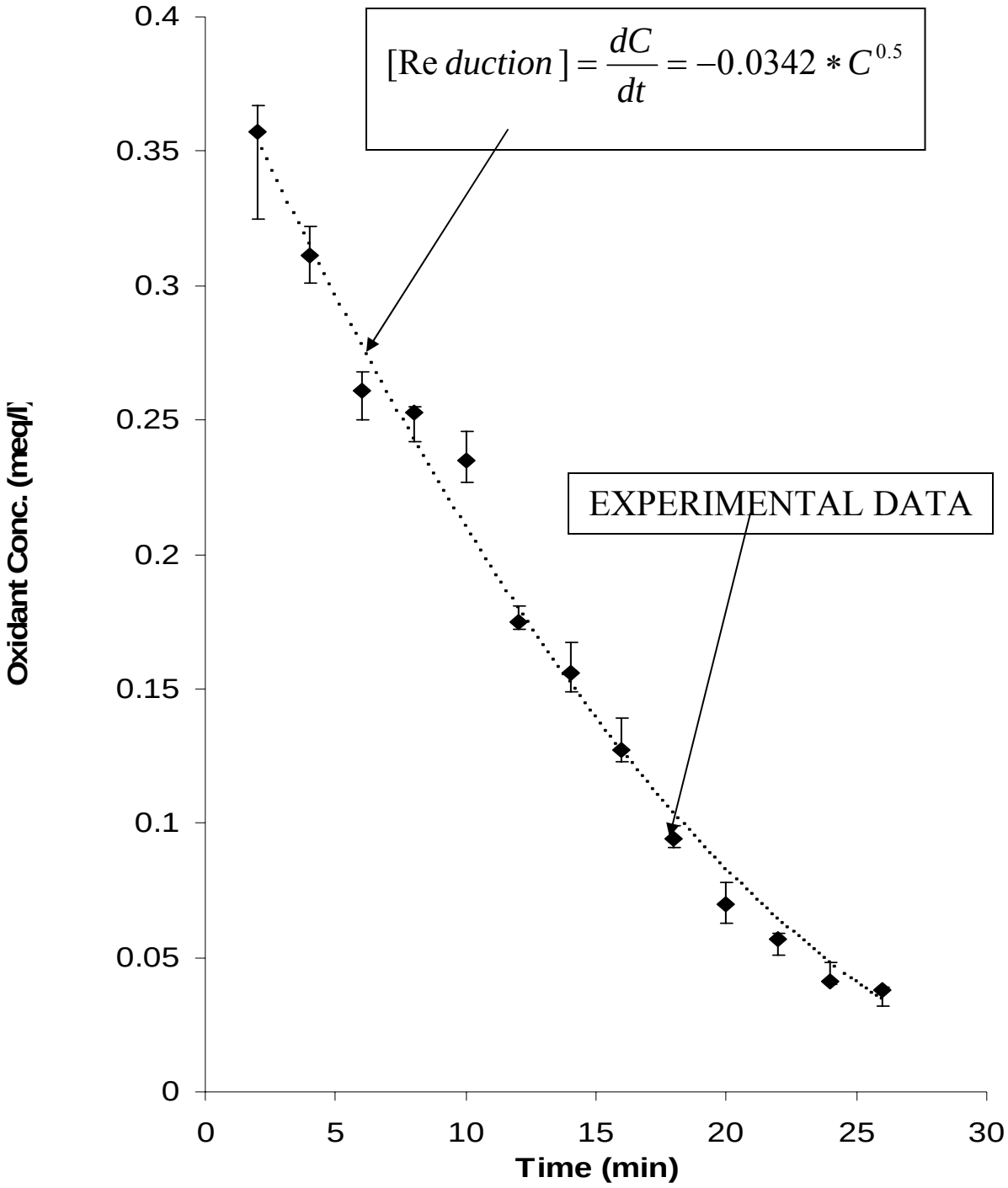

Figure 12: Comparison of Experimental Data and Determined Fitting Model for Reduction

4.1.3 Rate of Generation Kinetics Determination

Input energy was read during the experiment and the power input is calculated from the equation:

$$P = \frac{E}{t} \tag{21}$$

P = power input (kW)

E = energy input (J)

t = time (s)

The energy is function of the voltage and it is determined with the equation:

$$E = V * A * t \tag{22}$$

V = voltage (volts)

A = Amperage (amps)

The result of the calculation for the power input is given in Table 5.

At the beginning of the experiments, it can be assumed that [Rate of Accumulation] ≈ 0 and [Decay] ≈ 0, and that dC/dt for initial data is proportional to [Rate of Generation]. If it is that dC/dt slopes along the curve for the initial data (data from Figure 8. and Figure 9), then the best fitting model for V*dC/dt versus power can be found and in that way the [Rate of Generation] versus power can be determined. Calculation for V*dC/dt is given in Table 5. To fit this data two models were used. Model I is $A * P^n / (B+P^n)$ and model II is $A * (1-10^{-B*P})$. The values of the constants for Model I were determined: A = 1.17, B = 0.53 and n = 1.6. The values of constants for Model II were determined: A = 1.125 and B = 0.46. This data are given in Table 5.

Table 5: Data for Different Fitting Models

Power(P) KW	V*dC/dt Meq/min	a*(P)^n/(b+(P)^n)	a*(1-10^(-b*p))
0	0	0	0
0.53	0.46	0.46	0.49
0.70	0.59	0.58	0.59
0.86	0.68	0.68	0.67
1.01	0.74	0.75	0.74
1.03	0.77	0.76	0.75
1.33	0.87	0.86	0.85
1.70	0.93	0.94	0.94
2.00	0.98	0.99	0.99
2.20	1.01	1.00	1.01
2.50	1.05	1.04	1.04

In Figure 13 experimental data and data calculated from two models are plotted together. Generally, both models fit the data very well, but Model I fits better. It can be assumed that:

$$[\text{Rate of Generation}] = \frac{A * P^n}{B + P^n} \tag{23}$$

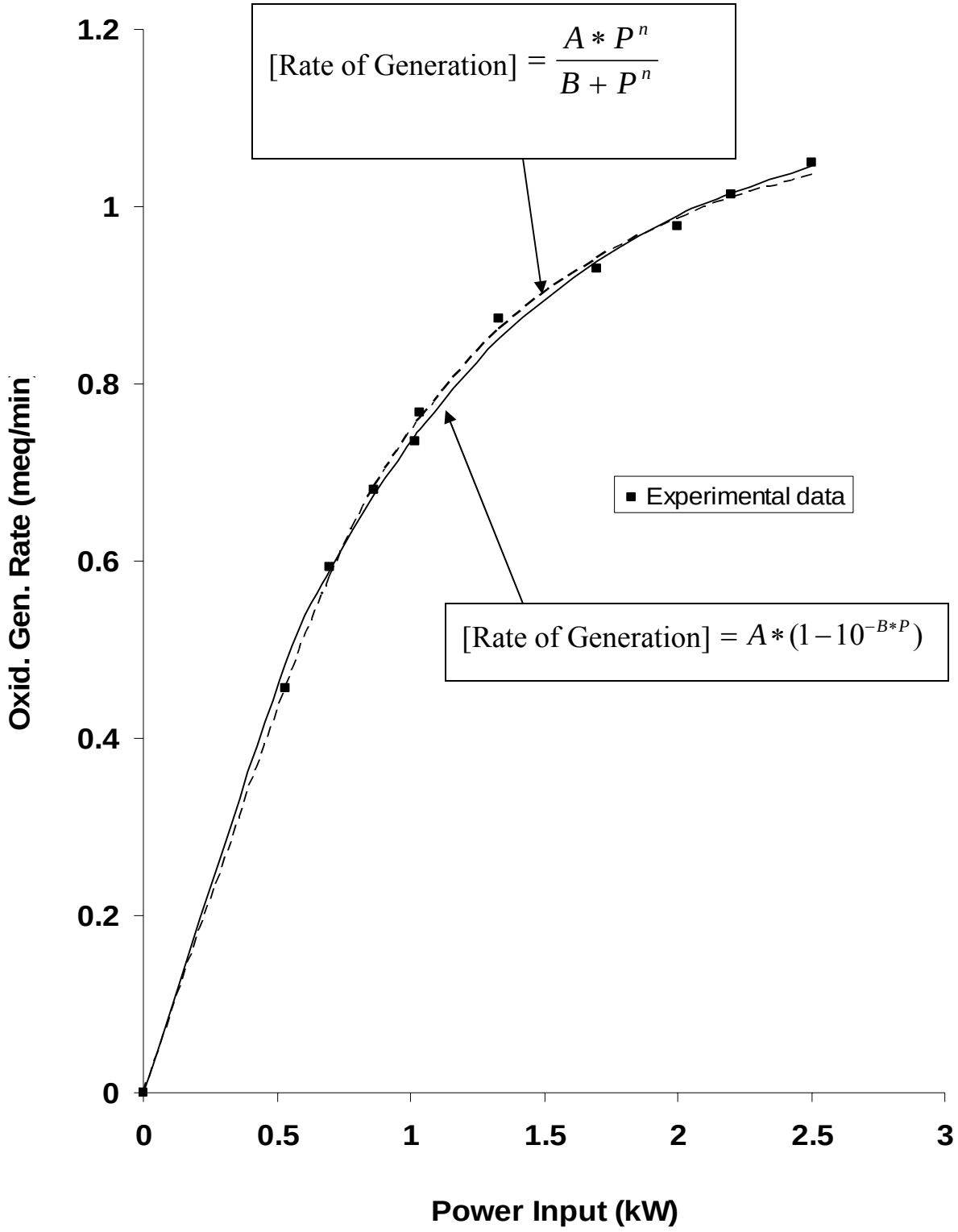

Figure 13: Oxidant Generation Rate versus Power Input

4.1.4 Determination of Concentration versus Time from Material Balance

From equations (16), (20) and (23):

$$V\frac{dC}{dt} = \frac{A * P^{1.6}}{B + P^{1.6}} - k_d * C^{1/2} * V \tag{24}$$

V = volume of fluid in the system (l)

Equation (24) can be written:

$$\frac{dC}{dt} = \frac{A * P^{1.6}}{B + P^{1.6}} * \frac{1}{V} - k_d * C^{1/2} \tag{25}$$

If we define K as:

$$K = \frac{A * P^{1.6}}{B + P^{1.6}} * \frac{1}{V} \tag{26}$$

The differential equation can be solved for C = 0 and t = 0:

$$t = -\frac{2 * K}{k_d^2} * LN\left(1 - \frac{k_d}{K} * C^{1/2}\right) - \frac{2}{k_d} * C^{1/2} \tag{27}$$

Equation (27) is the best fitting analytical (mathematical) model that connects concentration with time. The differential equation can be solved analytically only like time versus concentration.

Now, experimental data can be compared with derived model by plotting data at the same figure. In Figure 13 sets of data are provided that were run at 4 Hz and at different voltages

(power), and in Figure 14 sets of data are provided that were run at 8 Hz and different voltages (power). Looking carefully in Figure 13 and 14, it can be concluded that this model fits the data very well, especially for larger values of concentration. The differences between the experimental data and the derive model increase, when the concentration data and time decrease. One of the reasons for this is probably that the derived model is sensitive at small values of concentration, especially for small values under natural logarithm in the equation (27). Then, some assumptions of the model can increase the error, and, finally, measurement error in the experimental data probably increases for small values of concentration.

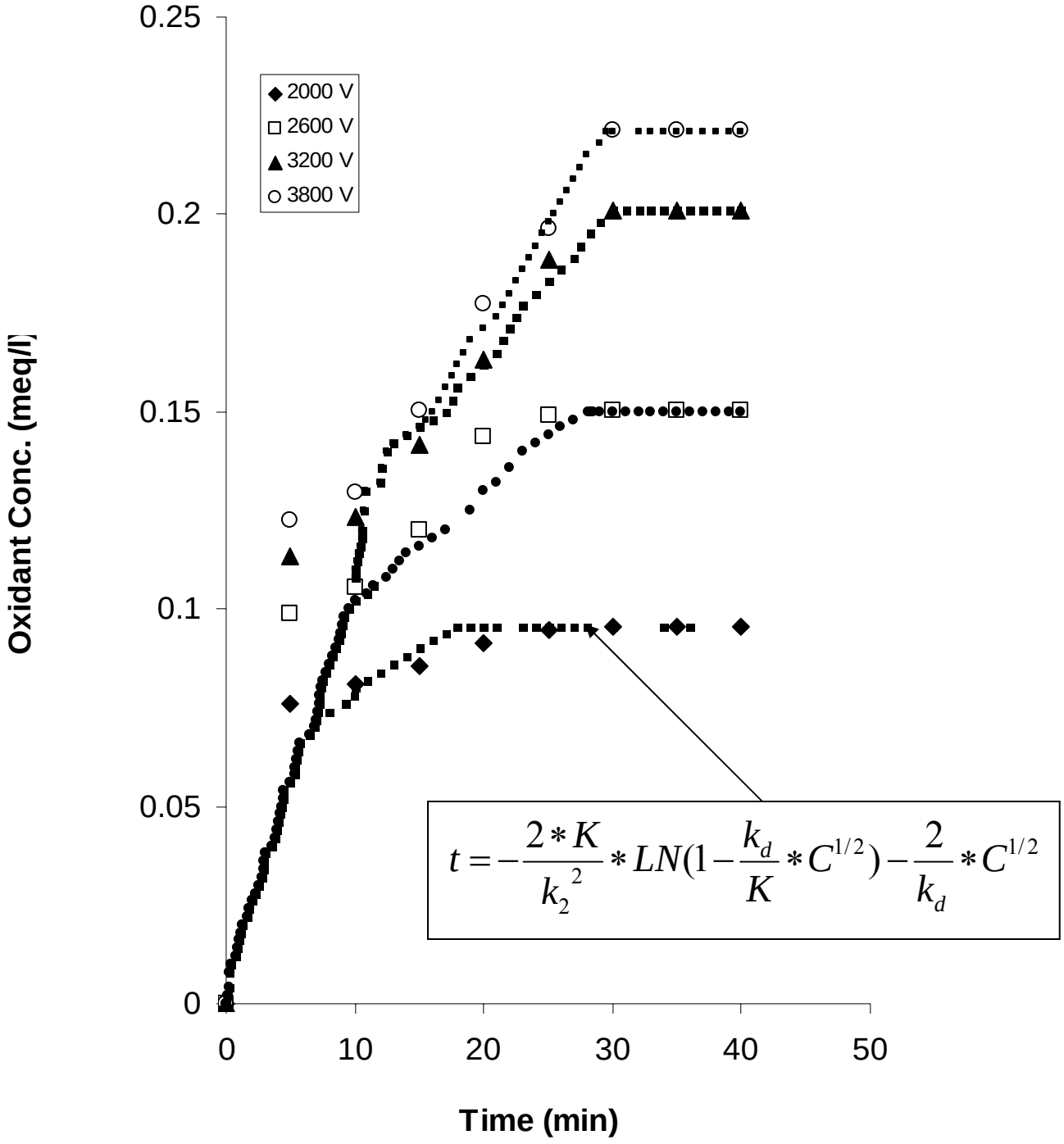

Figure 14: Comparison of Experimental Data and Final Determined Fitting Model at 4 Hz

4.2 CALCIUM REMOVAL FROM WATER WITH OXIDANT

This set of experiments was designed to show that adding oxidant radicals to the water as they were produced by the PUV equipment or the Ozonator (or both simultaneously), can remove calcium from the water. For the first set of experiments, bulk solution of $Ca(HCO_3)_2$ (prepared from a mixture of $NaHCO_3$ and $CaCl_2$)was the source of Ca in the water. For the second set of experiments University of Pittsburgh cooling tower water was used as the source of calcium in the water. Cooling tower water has pH = 7.3 and the concentration of calcium is about 165 mg/l. Cooling tower water also contains EDTA, complex that is used for the removal of hardness. All experiments were run at 4800V and 8 Hz (maximum power available) using PUV equipment. All oxidant concentrations in this set of experiments were represented as meq/l of oxidants as oxygen. For both sets of experiments open system with two reservoirs was used as Figure 15 shows.

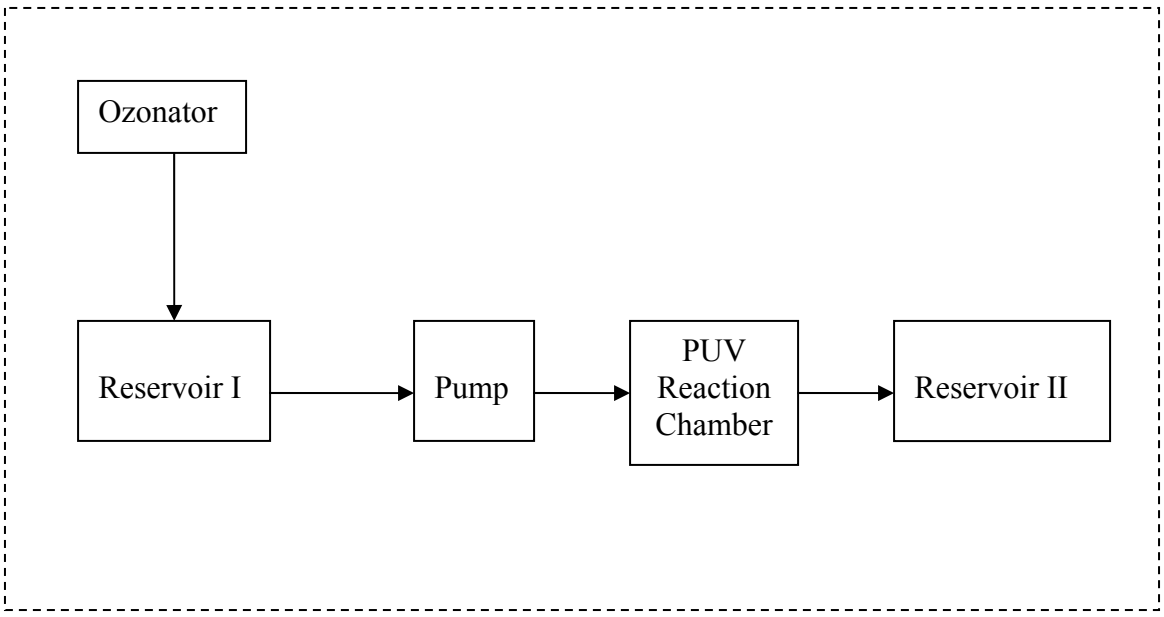

Figure 15: Experiment Design for Experiment of Calcium Removal

Reservoir I contains water with calcium that needs to be treated. Ozone from the Ozonator was placed in the system by connect to reservoir I and oxidant from the PUV equipment was added to the system via the reaction chamber. The volume of the first reservoir is 35 liters and

the volume of the second reservoir is 100 liters. The flow through the system is 0.1 gal /min and the volume of the reaction chamber is 1.75 gallons. Detention time in the reaction chamber is 17.5 min. For both sets of experiments (bulk solution and cooling tower water), the three experiments were run: a) using only the PUV equipment b) using only the Ozonator c) using the Ozonator and the PUV equipment simultaneously.

Before starting every experiment a control (blank) experiment was run without putting oxidant in the system and the concentration of calcium was measured in the same way as during the experiment. The next step, before beginning the experiment, was to obtain a sample from reservoir I and measure the starting concentration of calcium. During all experiments, it was measured the pH and range of pH was 7.1 - 7.4. At the same time, a temperature range of 20 °C - 25 °C was obtained. Also the concentration of oxidant added to the system in reservoir I by the Ozonator was measured and the amount was 8.5 meq /l as oxigen. All samples taken for measurement were divided into two parts, and one the half of the sample was not filtered (total calcium) and other half was filtered through the 0.2 μm membrane (soluble calcium). The concentrations of calcium for all samples were measured with AA.

Every experiment was run for 20 minutes before all equipment was shouted down and the first sample was taken from reservoir II (settling tank). Because the removal of calcium with oxidant is a relatively slow process, samples were also taken during of 24 hours, but after about 4 hours, the concentration didn't change anymore, and it can be concluded that the removal process for all experiments was finished within a period of 4 hours.

In reservoir II another process was also observed – the process of precipitation (sedimentation) for all experiments. After the experiment was finished white sediment was found at the bottom of reservoir. Samples of the sediment were taken for further analysis. The sediment was diluted with DI water and calcium concentration was measured in solution. It was found that the amount of calcium is 40% of sediment mass diluted in DI water and it was concluded that the content of sediment was $CaCO_3$ in all cases.

4.2.1 Experiment with Bulk Solution Using PUV light

In this experiment a bulk solution of calcium and only the PUV equipment were used. The experiment was conducted at 4800V and 8 Hz. The flow through system was 0.1 gal /min and the detention time in the reaction chamber was 17.5 min. Before beginning the experiment a control (blank) experiment was run that did not add oxidant to the system and the concentration of calcium was measured in same way as during the actual experiment. Before beginning the experiment, a sample from reservoir I and the starting concentration of calcium was measured. During the experiment pH was measured and the range of pH was 7.1 - 7.4. At the same time, the temperature was measure and the range during the experiment was 20 °C - 25 °C. All samples taken for measurements were divided into two parts and one the half of the sample was not filtered and other half was filtered through the 0.2 μm membrane. The concentration of calcium for all samples was measured with AA. The experiment was run for 20 minutes before all equipment was shouted down and the first sample was taken from reservoir II. The experiment was finished after a period of 4 hours.

Results are given in Table 6 and represented in Figure 16. Data in Figure 16 are represented as the data with filtration and the data without filtration. It can be concluded from the experimental data that under those conditions PUV light can remove calcium from water. When starting concentration of calcium is about 450 mg/l, removal of calcium is about 60 mg/l under these experimental conditions.

Table 6: Removal of Dissolved Calcium Using PUV Light for Bulk Solution

Time min	Sample Without Filtration mg/L	Sample With Filtration mg/L
0	453	453
20	450	439
50	441	433
80	427	415
110	418	408
140	404	400
240	395	394
1440	395	394

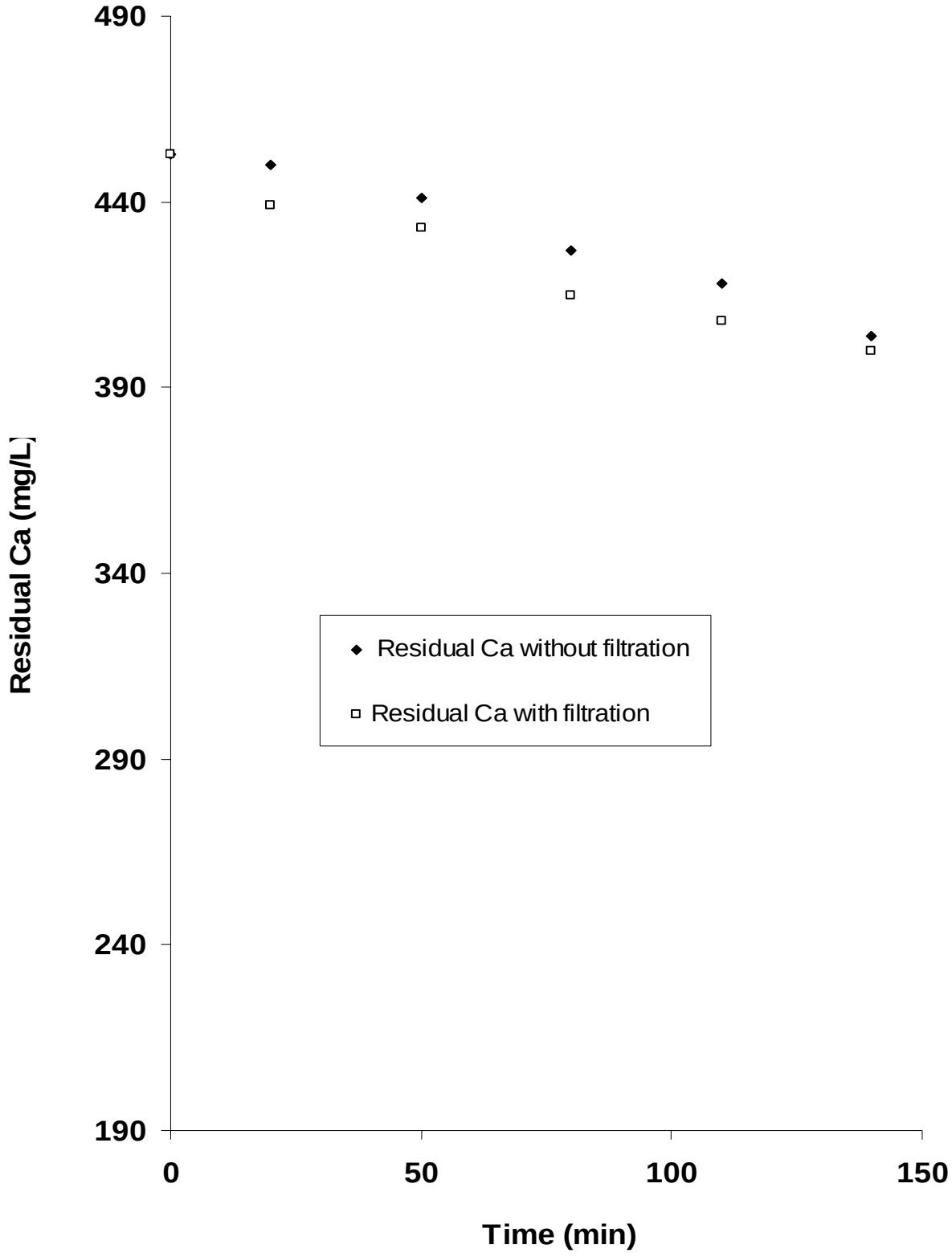

Figure 16: Removal of Dissolved Calcium Using PUV Light for Bulk Solution

4.2.2 Experiment with Bulk Solution Using Ozonator

In this experiment a bulk solution of calcium and only the Ozonator were used. The experiment was conducted at 4800V and 8 Hz. The flow through system was 0.1 gal /min and the detention time in the reaction chamber was 17.5 min. Before beginning the experiment a control (blank) experiment was run that did not add oxidant to the system and the concentration of calcium was measured in same way as during the actual experiment. Before beginning the experiment, a sample from reservoir I and the starting concentration of calcium was measured. During the experiment pH was measured and the range of pH was 7.1 - 7.4. At the same time, the temperature was measure and the range during the experiment was 20 °C - 25 °C. All samples taken for measurements were divided into two parts and one the half of the sample was not filtered and other half was filtered through the 0.2 μm membrane. The concentration of calcium for all samples was measured with AA. The experiment was run for 20 minutes before all equipment was shouted down and the first sample was taken from reservoir II. The experiment was finished after a period of 4 hours.

Results are given in Table 7 and represented in Figure 17. Data in Figure 17 are represented as the data with filtration and the data without filtration. It can be concluded from the experimental data that under those conditions PUV light can remove calcium from water. When starting concentration of calcium is about 440 mg/l, removal of calcium is about 155 mg/l under these experimental conditions.

Table 7: Removal of Dissolved Calcium Using Ozonator for Bulk Solution

Time min	Sample Without Filtration mg/L	Sample With Filtration mg/L
0	440	440
20	439	414
50	387	369
80	350	339
110	316	309
140	289	286
240	287	285
1440	285	285

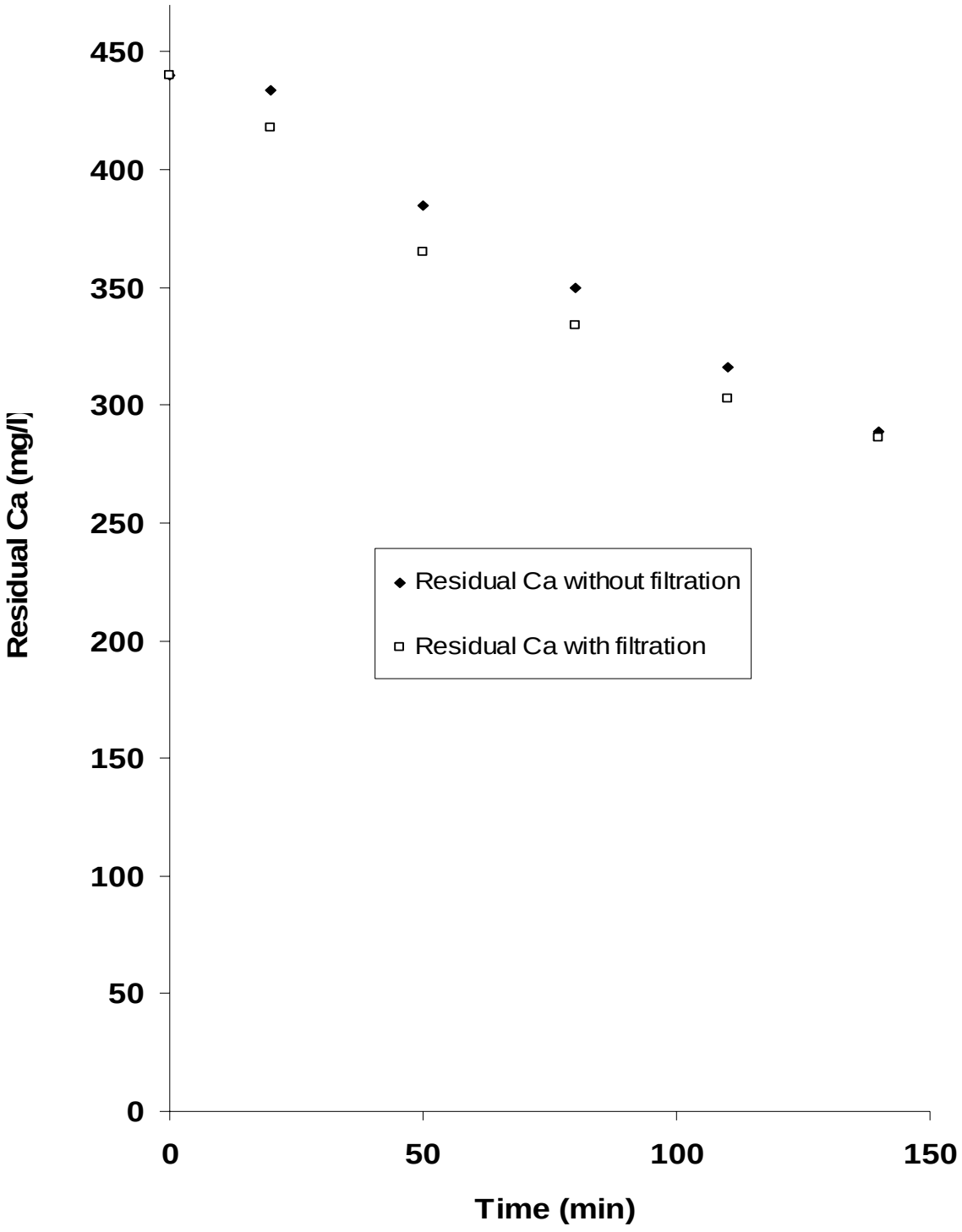

Figure 17: Removal of Dissolved Calcium Using Ozonator for Bulk Solution

4.2.3 Experiment with Bulk Solution Using Ozonator and PUV Light

In this experiment a bulk solution of calcium and Ozonator with PUV equipment were used. The experiment was conducted at 4800V and 8 Hz. The flow through system was 0.1 gal /min and the detention time in the reaction chamber was 17.5 min. Before beginning the experiment a control (blank) experiment was run that did not add oxidant to the system and the concentration of calcium was measured in same way as during the actual experiment. Before beginning the experiment, a sample from reservoir I and the starting concentration of calcium was measured. During the experiment pH was measured and the range of pH was 7.1 - 7.4. At the same time, the temperature was measure and the range during the experiment was 20 °C - 25 °C. All samples taken for measurements were divided into two parts and one the half of the sample was not filtered and other half was filtered through the 0.2 μm membrane. The concentration of calcium for all samples was measured with AA. The experiment was run for 20 minutes before all equipment was shouted down and the first sample was taken from reservoir II. The experiment was finished after a period of 4 hours.

Results are given in Table 8 and represented in Figure 18. Data in Figure 18 are represented as the data with filtration and the data without filtration. It can be concluded from the experimental data that under those conditions PUV light can remove calcium from water. When starting concentration of calcium is about 450 mg/l, removal of calcium is about 255 mg/l under these experimental conditions.

Table 8: Removal of Dissolved Calcium Using PUV Light + Ozonator for Bulk Solution

Time min	Sample Without Filtration mg/L	Sample With Filtration mg/L
0	449	449
20	401	396
50	351	327
80	295	275
110	244	233
140	199	195
240	196	194
1440	195	194

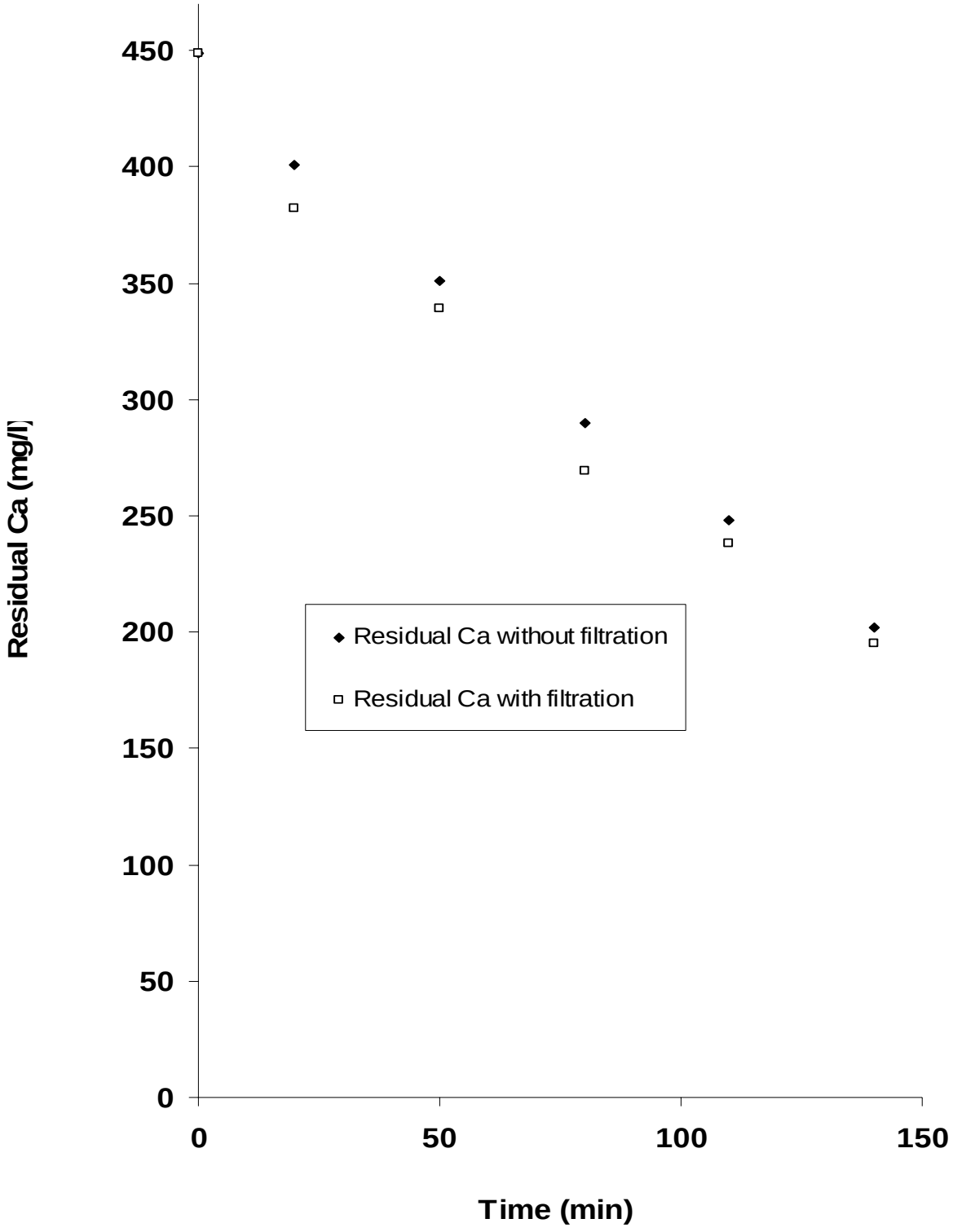

Figure 18: Removal of Dissolved Calcium Using PUV Light + Ozonator for Bulk Solution

4.2.4 Removal of Ca for Different Treatment Conditions for Bulk Solution

The results from all three experiments are plotted together in Figure 19. It can be clearly concluded from Figure 19 that the best removal of calcium is by using the Ozonator with PUV equipment, because it was added the largest amount of oxidant to the system. There is a slightly less removal of calcium using only the Ozonator, and the smallest level of removal results from using only the PUV equipment.

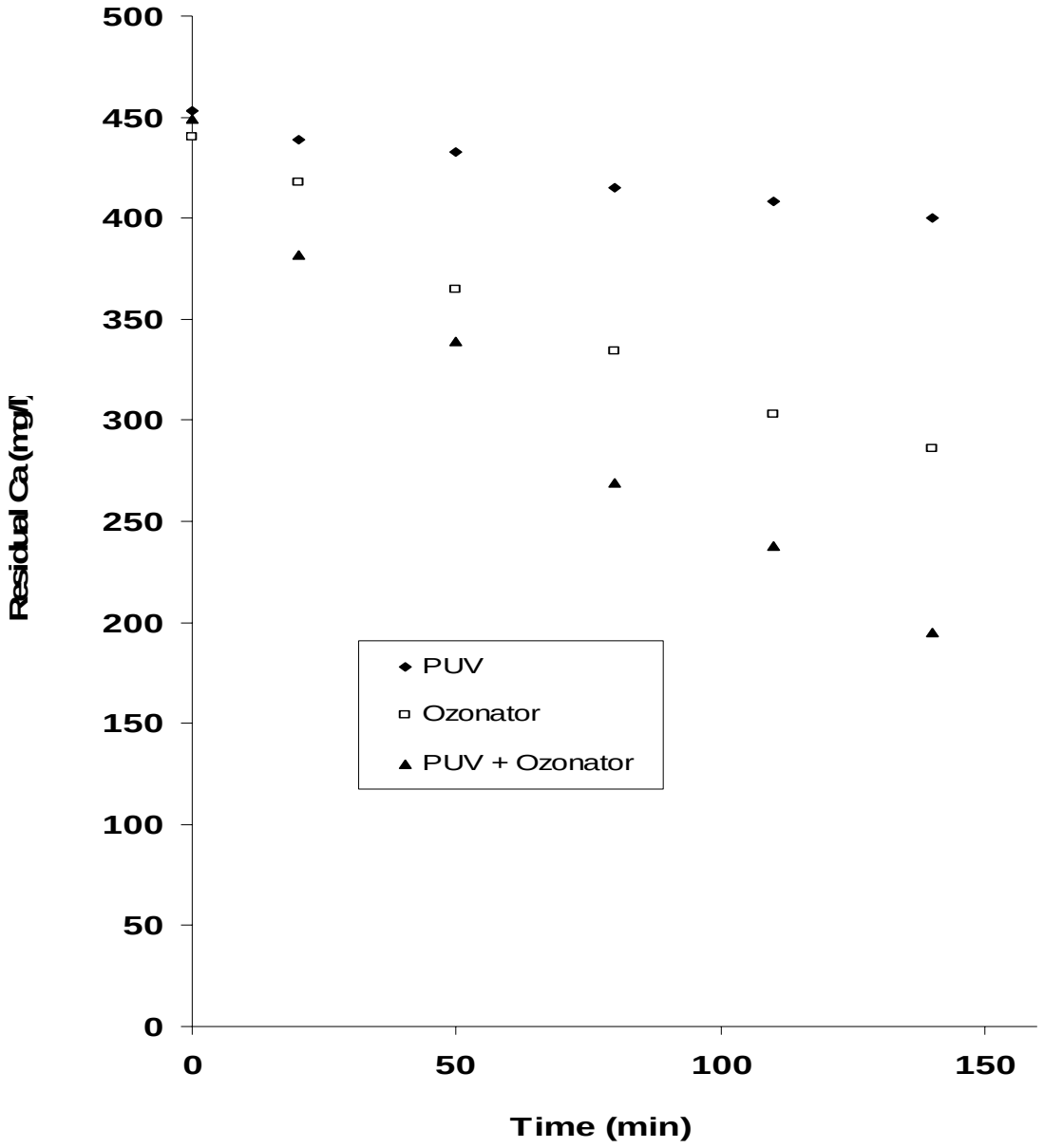

Figure 19: Removal of Dissolved Calcium from Bulk Solution for Different Condition

4.2.5 Kinetics of Removal of Ca for Bulk Solution

The data from all three experiments, from Figure 19 is plotted as a semi – log graph in Figure 20. It can be concluded from Figure 20 that for all three experiments, the results form a straight line on a semi – log graph and indicate that the kinetics of removal; it is a first order reaction which can be defined:

$$\frac{dC}{dt} = -k * C \tag{28}$$

k = reaction constant for system with bulk solution (min^{-1})

C = concentration of removed calcium from bulk solution (mg/l)

t = time of removal in settling tank with bulk solution (min)

The reaction constant is different for different experimental conditions. A base for a reaction constant is a natural logarithm. For the experiment with only the PUV light, the reaction constant is $k_1 = 0.001$. For experiment with only the Ozonator, reaction constant is $k_2 = 0.0031$. For the experiment with the Ozonator and the PUV equipment, the reaction constant is $k_3 = 0.0059$. Substituting k_1 and k_2, the value is 0.0041, and that is less than $k_3 = 0.0059$. It can be concluded that the synergetic effect of PUV light and the Ozonator during the experiment produce a better removal of Ca than each separate experiment did using only the PUV equipment or only the Ozonator.

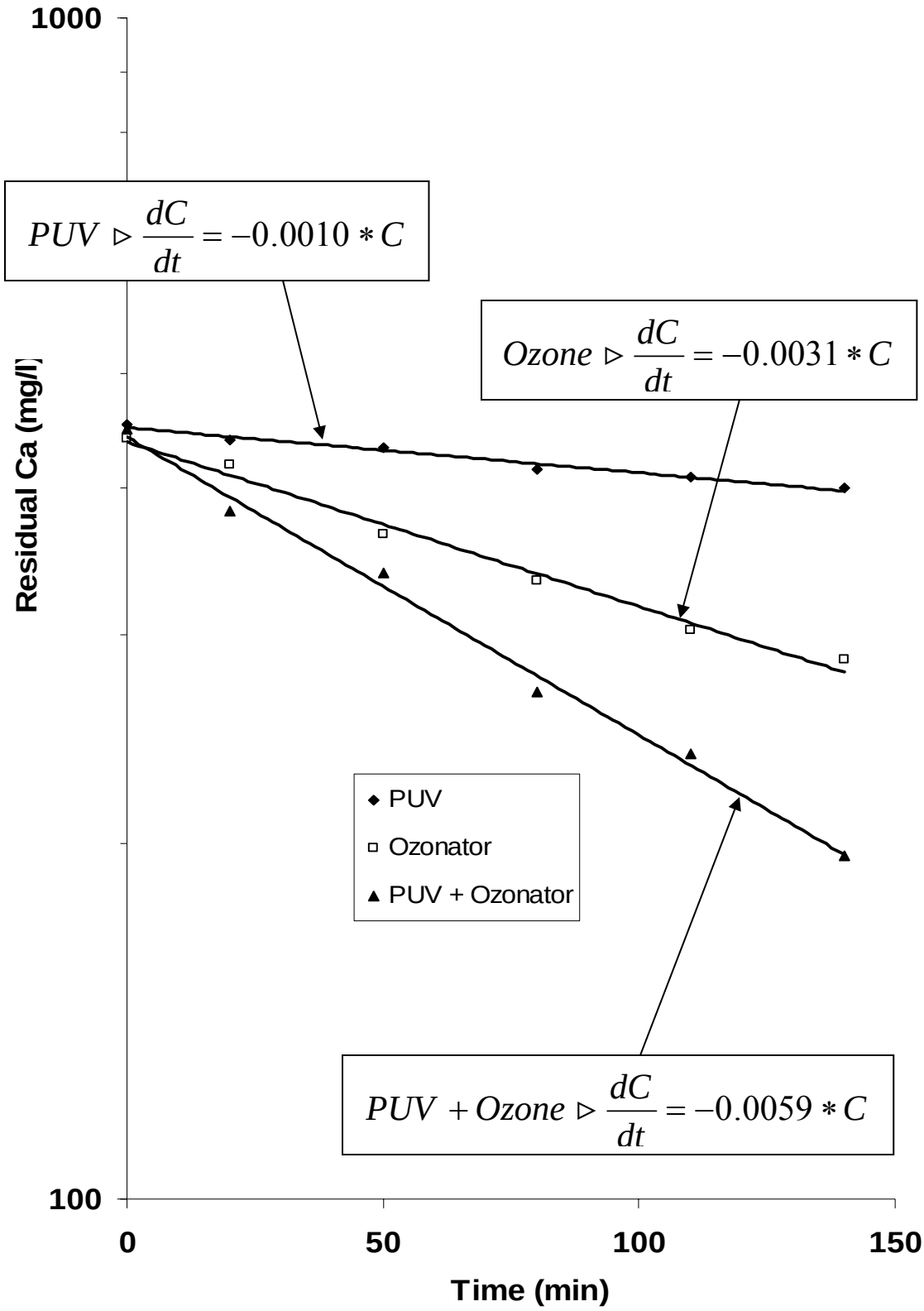

Figure 20: Removal of Dissolved Calcium from Bulk Solution at Semi - Log Graph

4.2.6 Experiment with Cooling Tower Water Using PUV Light

In this experiment University of Pittsburgh cooling tower water was used as the source of calcium treated with the PUV equipment. The experiment was conducted at 4800V and 8 Hz. The flow through system was 0.1 gal /min and the detention time in the reaction chamber was 17.5 min. Before beginning the experiment a control (blank) experiment was run that did not add oxidant to the system and the concentration of calcium was measured in same way as during the actual experiment. Before beginning the experiment, a sample from reservoir I and the starting concentration of calcium was measured. During the experiment pH was measured and the range of pH was 7.1 - 7.4. At the same time, the temperature was measure and the range during the experiment was 20 °C - 25 °C. All samples taken for measurements were divided into two parts and one the half of the sample was not filtered and other half was filtered through the 0.2 μm membrane. The concentration of calcium for all samples was measured with AA. The experiment was run for 20 minutes before all equipment was shouted down and the first sample was taken from reservoir II. The experiment was finished after a period of 4 hours.

Results are given in Table 9 and represented in Figure 21. Data in Figure 21 are represented as the data with filtration and the data without filtration. It can be concluded from the experimental data that under those conditions PUV light can remove calcium from water. When starting concentration of calcium is about 166 mg/l, removal of calcium is about 40 mg/l under these experimental conditions.

Table 9: Removal of Dissolved Calcium Using PUV Light with Cooling Tower Water

Time min	Sample Without Filtration mg/L	Sample With Filtration mg/L
0	166	166
20	163	160
50	154	150
80	146	142
110	138	134
140	129	127
240	126	125
1440	126	125

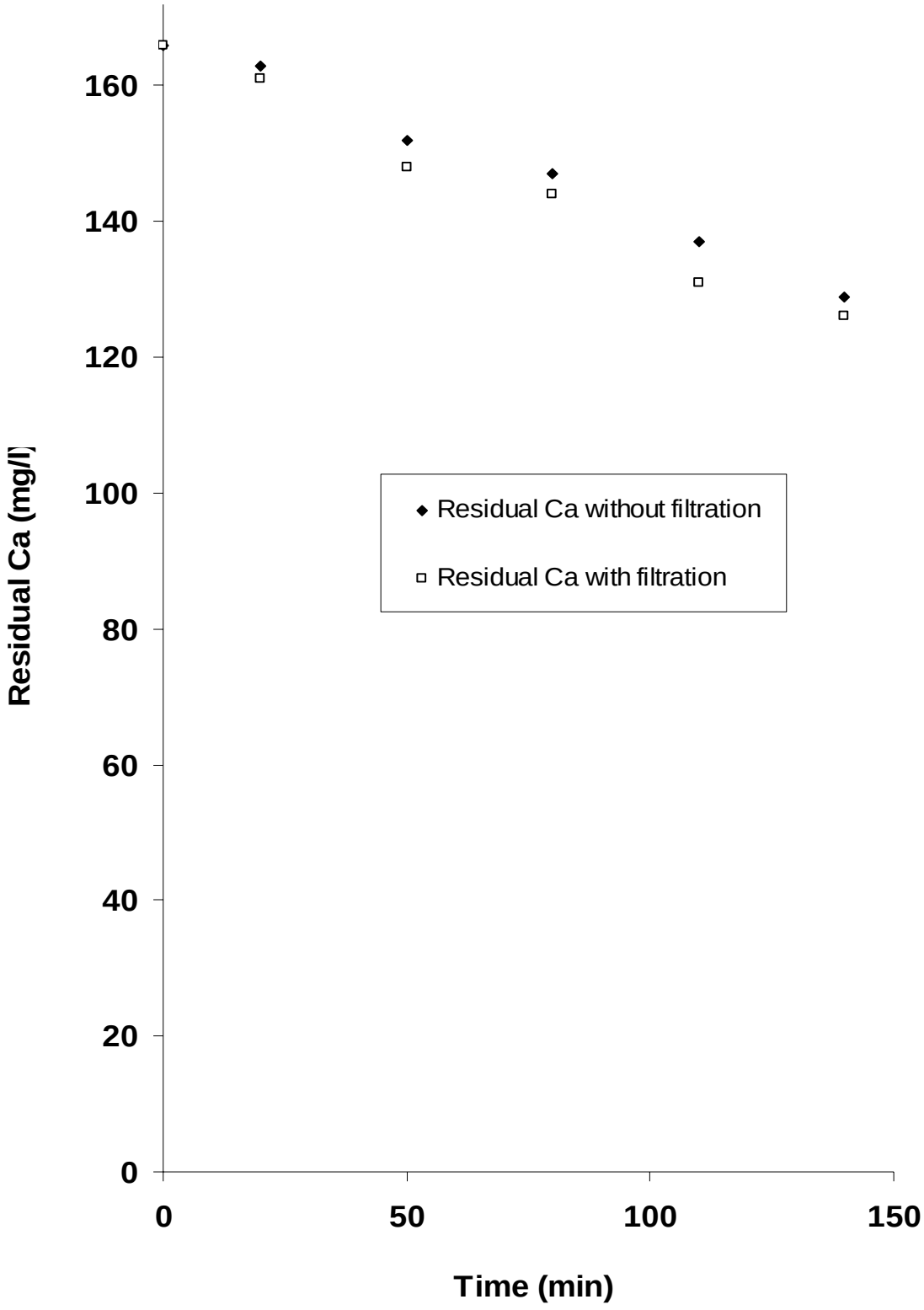

Figure 21: Removal of Dissolved Calcium Using PUV Light with Cooling Tower Water

4.2.7 Experiment with Cooling Tower Water Using Ozonator

In this experiment University of Pittsburgh cooling tower water was used as the source of calcium treated with the Ozonator. The experiment was conducted at 4800V and 8 Hz. The flow through system was 0.1 gal /min and the detention time in the reaction chamber was 17.5 min. Before beginning the experiment a control (blank) experiment was run that did not add oxidant to the system and the concentration of calcium was measured in same way as during the actual experiment. Before beginning the experiment, a sample from reservoir I and the starting concentration of calcium was measured. During the experiment pH was measured and the range of pH was 7.1 - 7.4. At the same time, the temperature was measure and the range during the experiment was 20 °C - 25 °C. All samples taken for measurements were divided into two parts and one the half of the sample was not filtered and other half was filtered through the 0.2 μm membrane. The concentration of calcium for all samples was measured with AA. The experiment was run for 20 minutes before all equipment was shouted down and the first sample was taken from reservoir II. The experiment was finished after a period of 4 hours.

Results are given in Table 10 and represented in Figure 22. Data in Figure 22 are represented as the data with filtration and the data without filtration. It can be concluded from the experimental data that under those conditions PUV light can remove calcium from water. When starting concentration of calcium is about 167 mg/l, removal of calcium is about 70 mg/l under these experimental conditions.

Table 10: Removal of Dissolved Calcium Using Ozonator with Cooling Tower Water

Time min	Sample Without Filtration mg/L	Sample With Filtration mg/L
0	167	167
20	163	155
50	150	138
80	134	122
110	118	110
140	101	98
240	100	98
1440	98	97

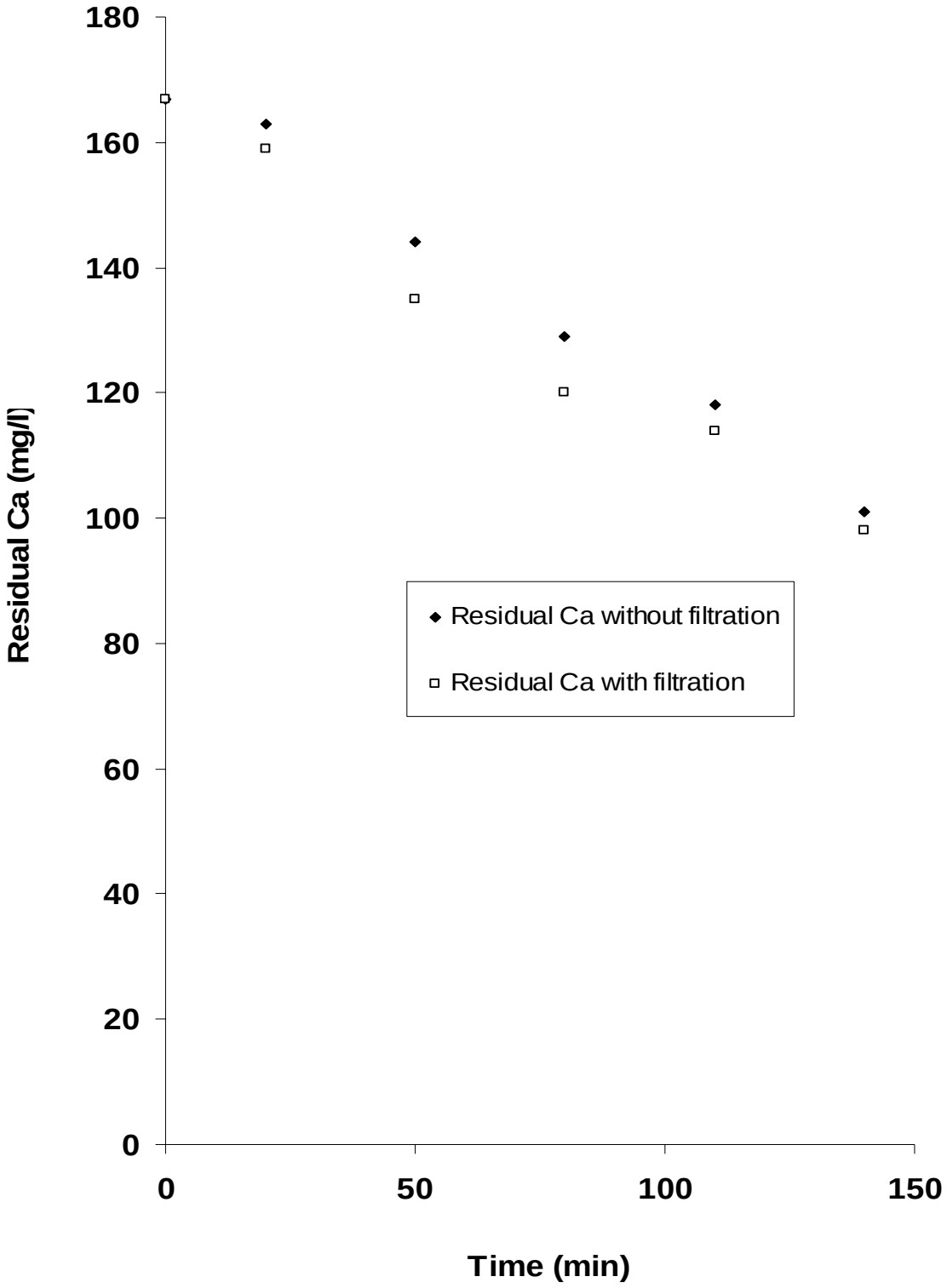

Figure 22: Removal of Dissolved Calcium Using Ozonator with Cooling Tower Water

4.2.8 Experiment with Cooling Tower Water Using Ozonator and PUV Light

In this experiment University of Pittsburgh cooling tower water was used as the source of calcium treated with the PUV equipment. The experiment was conducted at 4800V and 8 Hz. The flow through system was 0.1 gal /min and the detention time in the reaction chamber was 17.5 min. Before beginning the experiment a control (blank) experiment was run that did not add oxidant to the system and the concentration of calcium was measured in same way as during the actual experiment. Before beginning the experiment, a sample from reservoir I and the starting concentration of calcium was measured. During the experiment pH was measured and the range of pH was 7.1 - 7.4. At the same time, the temperature was measure and the range during the experiment was 20 °C - 25 °C. All samples taken for measurements were divided into two parts and one the half of the sample was not filtered and other half was filtered through the 0.2 μm membrane. The concentration of calcium for all samples was measured with AA. The experiment was run for 20 minutes before all equipment was shouted down and the first sample was taken from reservoir II. The experiment was finished after a period of 4 hours.

Results are given in Table 11 and represented in Figure 23. Data in Figure 23 are represented as the data with filtration and the data without filtration. It can be concluded from the experimental data that under those conditions PUV light can remove calcium from water. When starting concentration of calcium is about 169 mg/l, removal of calcium is about 115 mg/l under these experimental conditions.

Table 11: Removal of Dissolved Calcium Using PUV + Ozonator with Cool. Tower Water

Time min	Sample Without Filtration mg/L	Sample With Filtration mg/L
0	169	169
20	163	150
50	134	120
80	109	98
110	86	79
140	60	58
240	55	54
1440	54	54

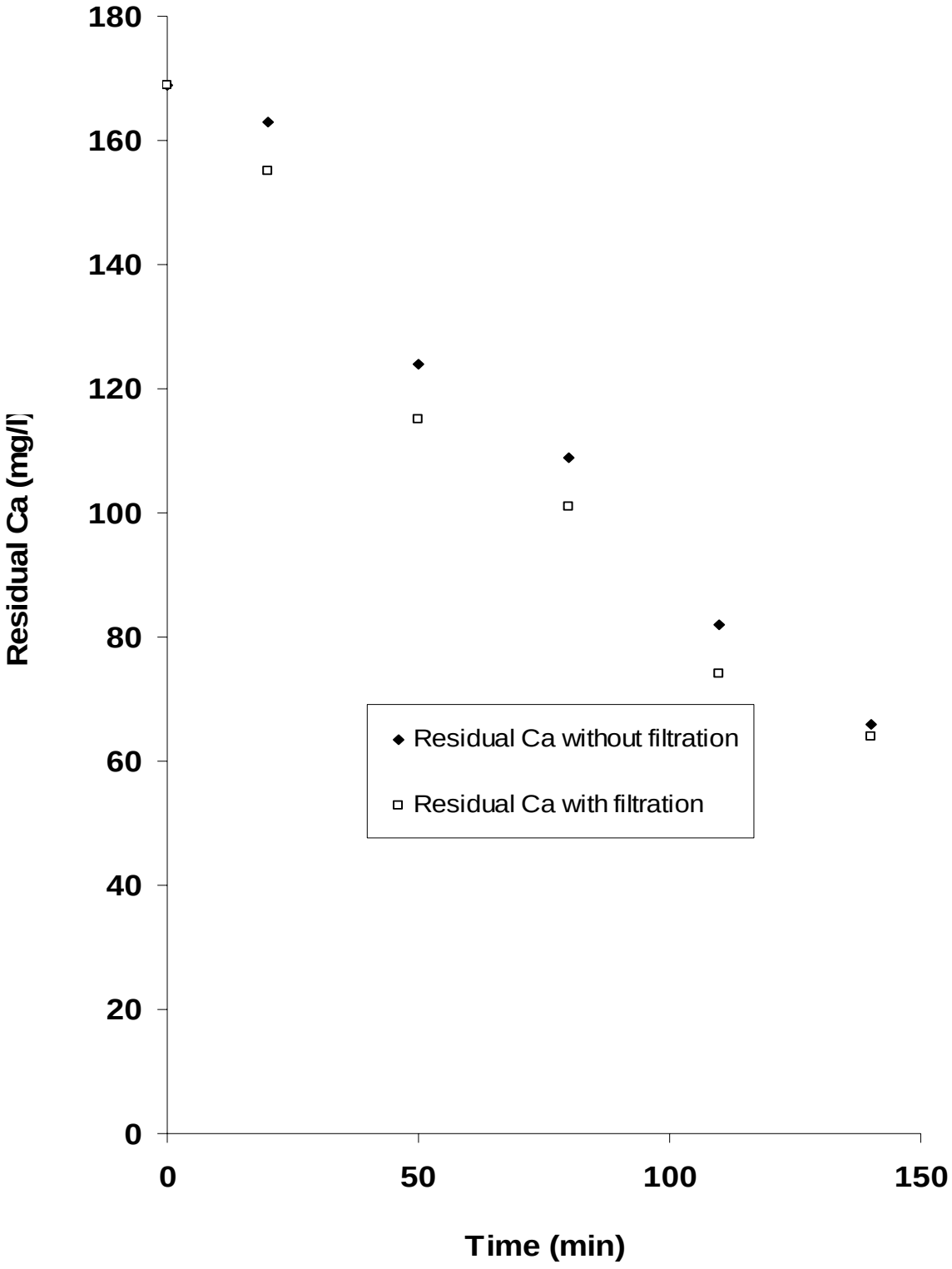

Figure 23: Removal of Dissolved Calcium Using PUV + Ozonator with Cool. Tower Water

4.2.9 Removal of Ca for Different Treatment Conditions for Cooling Tower Water

The results from all three experiments are plotted together in Figure 24. It can be clearly concluded from Figure 24 that the best removal of calcium is by using the Ozonator with PUV equipment, because it was added the largest amount of oxidant to the system. There is a slightly less removal of calcium using only the Ozonator, and the smallest removal occurred when using only the PUV equipment.

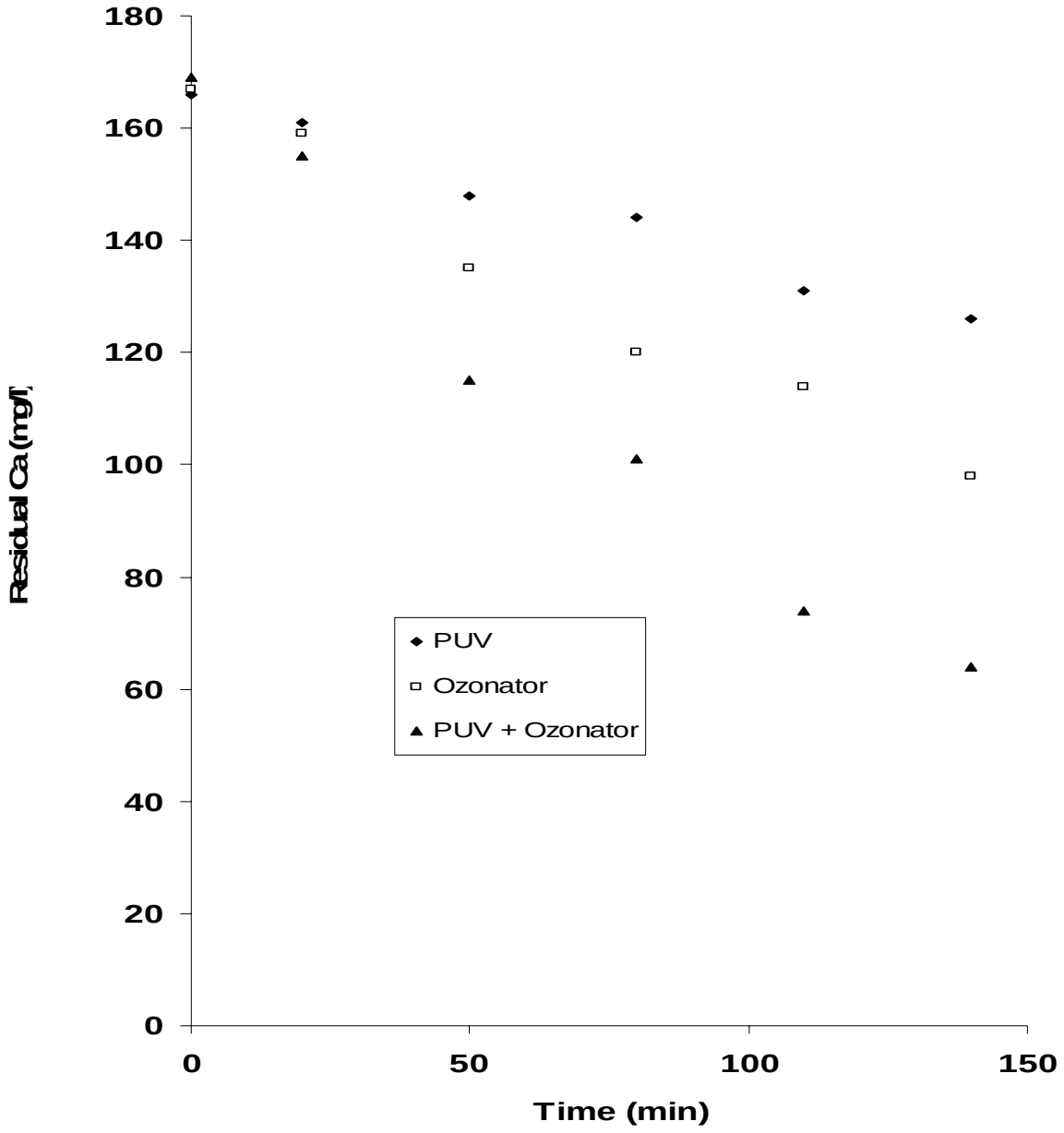

Figure 24: Removal of Dissolved Calcium from Cool. Tower Water for Different Condition

4.2.10 Kinetics of Calcium Removal for Cooling Tower Water

The data from all three experiments, from Figure 24 is plotted as a semi – log graph in Figure 20. It can be concluded from Figure 25 that for all three experiments, the results form a straight line on a semi – log graph and indicate that the kinetics of removal; it is a first order reaction which can be defined:

$$\frac{dC}{dt} = -k * C \tag{29}$$

k = reaction constant for system with cool. tower water (min^{-1})

C = concentration of remove calcium from cool. tower water (mg/l)

t = time of removal in settling tank with cool. tower water (min)

The reaction constant is different for different experimental conditions. A base for a reaction constant is a natural logarithm. For the experiment with only the PUV light, the reaction constant is $k_1 = 0.0019$. For experiment with only the Ozonator, reaction constant is $k_2 = 0.0038$. For the experiment with the Ozonator and the PUV equipment, the reaction constant is $k_3 = 0.0070$. Substituting k_1 and k_2, the value is 0.0057, and that is less than $k_3 = 0.0070$. It can be concluded that the synergetic effect of PUV light and the Ozonator during the experiment produce a better removal of Ca than each separate experiment did using only the PUV equipment or only the Ozonator.

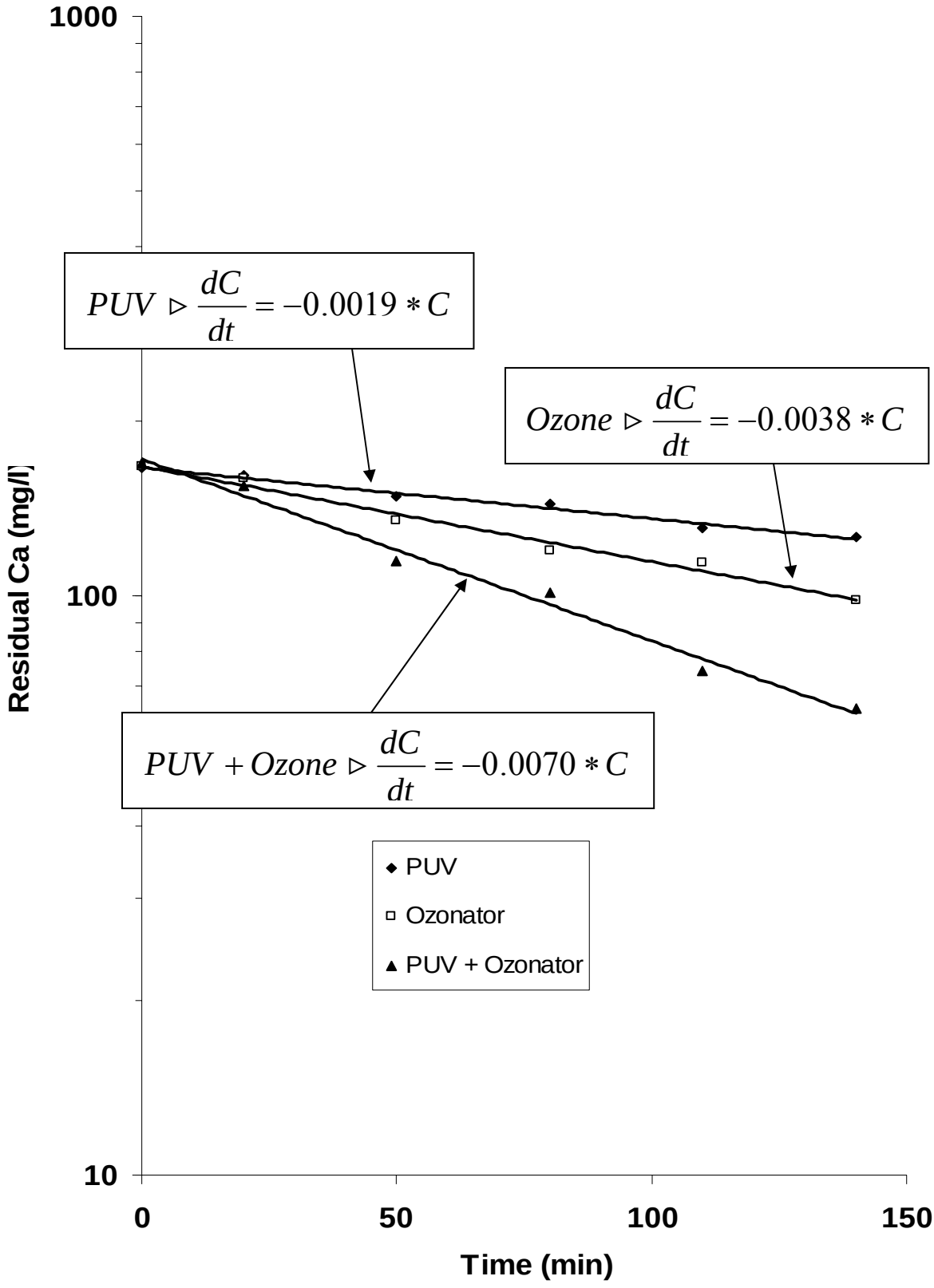

Figure 25: Removal of Dissolved Calcium from Cooling Tower Water at Semi - Log Graph

5.0 SUMMARY AND CONCLUSION

Pulsar UV system was evaluated for the treatment of water and the determination of the kinetics of oxidant radicals in water. Photons generated by the PUV are responsible for the destruction of target compounds and the photolysis of covalent bonds, and for the production of oxidant radicals that can be used for further treatment.

This work consists of two parts. First, equipment was designed to provide sets of experiments with purpose to determine the kinetics of oxidant radical production by the PUV equipment. Second, experiments were designed to determine whether oxidant radicals produce by the PUV equipment and the Ozonator can remove calcium from water.

Using PUV equipment the concentration of oxidant radicals versus time was measured. From the experimental results, it can be concluded that by increasing the power input (voltage, frequency), oxidant radicals production increases also. After some time, the system reaches a steady state and remains there. The material balance at steady state [Rate of Generation] = [Reduction] was found.

Experimental data for Reduction was measured. Next, the assumed differential equation for decay kinetics was solved. Using this solution, and by fitting it to the experimental data, the order of decay, n = 0.5, and the coefficient of reduction, k_d = -0.00342, with R^2 = 0.9906 were found. After comparison with the experimental data, it can be concluded that fitting this model is a good approximation for the experimental data.

The best fitting model for [Rate of Generation] was determined. It was assumed that for the initial data dC/dt ≈ [Rate of Generation], and for the same data, [Rate of Accumulation] ≈ 0 and [Decay] ≈ 0. After fitting the experimental data, the best model was found: [Rate of Generation] = $A*P^n/(B+P^n)$. The values of the constants are: A = 1.17, B = 0.53 and n = 1.6. After

comparison with the experimental data, it can be concluded that fitting the model for [Rate of Generation] is a good approximation of the experimental data.

Fitting models for [Reduction] and [Rate of Generation] were included in the material balance. The differential equation for material balance was solved and the final fitting model for time versus concentration of oxidant radicals was determined. This model was compared with the experimental data. Looking carefully, it can be concluded that the model fits the experimental data very well for larger values of concentration. For small values of concentration and time, error increases, probably because the model is sensitive to small values of concentration (the natural logarithm in the equation), the error of the experimental measurements also increases with smaller values, and some model assumptions can increase error at smaller concentration.

The experiments with calcium removal were designed to use two sources of calcium: bulk solution and cooling tower water. For both sources, three experiments were designed: a) using only the PUV equipment b) using only the Ozonator and c) using the Ozonator + PUV equipment.

During the experiments a pH of 7.1 -7.4 and a temperature 20 °C – 25 °C were measured. This is important because the experiments needed to remove calcium using oxidant in water, not because of changing pH and temperature. The removal of calcium continued in reservoir II for four hours accomplished by a process of precipitation. It was determined that the content of the sediment was $CaCO_3$. The concentration of oxidant added to the system by the Ozonator was 8.5 meq/l.

Using a bulk solution as the source of calcium, the removal of calcium was measured: 1) using the PUV light removal was 60 mg/l, 2) using the Ozonator removal was 155 mg/l, and 3) using the PUV light and the Ozonator together the removal was 255 mg/l.

Using the coling tower water as the source of calcium, the removal of calcium was measured: 1) using the PUV light the removal was 40 mg/l, 2) using the Ozonator the removal was 70 mg/l. and 3) using the PUV light and the Ozonator the removal was 115 mg/l.

The data were plotted as a semi – log graph, and it can be concluded that the reaction of calcium removal is a first order reaction. For the bulk solution 1) using only the PUV light, k_1 = 0.001, 2) using only the Ozonator, k_2 = 0.0031 and 3) using the PUV light and the Ozonator, k_3 = 0.0059. The synergetic effect of the PUV light and the Ozonator working together on a bulk

solution accomplishes better removal of calcium than each separate experiment because $k_1 + k_2 < k_3$.

For the solution with cooling tower water 1) using the PUV light, $k_1 = 0.0019$, 2) using the Ozonator, $k_2 = 0.0038$ and 3) using the PUV light and the Ozonator, $k_3 = 0.0070$. The synergetic effect of the PUV light and the Ozonator working together using cooling tower water accomplishes better removal of calcium than each separate experiment because $k_1 + k_2 < k_3$.

The reaction constants for tap water and cooling tower water for different experimental conditions are given in table 12:

Table 12: Reaction constants for different experimental conditions

Water	k (PUV)	k (Ozone)	k (Ozone + PUV)
Tap Water	0.0010	0.0031	0.0059
Cooling Tower	0.0019	0.0038	0.0070

Looking at all the experimental data, it can be concluded that the difference between removal of calcium with filtration (soluble calcium) and removal of calcium without filtration (total calcium) is negligible. This indicates that removal of calcium by oxidant is very quick process, but later the system needs some time for precipitation of $CaCO_3$. Probably reason for precipitation of $CaCO_3$ is that OH radicals react with bicarbonate ions in the reaction: $OH\bullet + HCO_3^- = CO_3^{2-} + H_2O$. The excess carbonate ions react with calcium ions and probably move the chemical reaction equilibrium in way of calcium carbonate precipitation (sedimentation) without significant changing of a pH in the solution.

6.0 RECOMMENDATIONS FOR FUTURE WORK

This work proved that PUV technology can produce oxidant radicals in water and that oxidant radicals can be used for the removal of calcium. The recommendations for future work are to design future research and experiments with larger detention time and higher energy input for the removal of calcium from water and to determine whether this process can be efficient and feasible, and to determine whether it can be used in industry. Simultaneously, it can be determined whether PUV equipment can remove magnesium from water or whether hardness can be removed from water using PUV equipment.

The removal of other metals from water, such as iron or manganese can be tested and feasibility of the PUV system for ground water treatment can be verified. In addition, the process of disinfection can be tested for different experimental conditions with different turbidity of water. The removal of organic compounds, such as EDTA, MTBE and BTEX using the PUV technology can be examined, and the feasibility of PUV determined. In the same manner, its use with halogen - organic compounds can be tested also.

The removal of several contaminants at the same time, such as metals and organic compounds, should also be tested. Water with high turbidity should be investigated and the use of the PUV equipment for treatment of waste water should be assessed. At the same time, other oxidants (ozone, peroxide, etc) can be added to determine if that increases the efficiency of the process. The best ratio of oxidant produced by PUV equipment while other oxidants are added to the system for maximum efficiency of the process should also be determined.

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